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FOREWORD

The hearty reception accorded the appearance in February of Volume I of the SURVEY has been most gratifying to those who have participated in its compilation.

The Division of Chemistry and Chemical Technology of the National Research Council is convinced that a series of this type may serve an admirable purpose in bringing the critical opinions of our best known chemists directly to the attention of our young investigators. To this end the Division has now enlisted the services of additional authors in order that Volume II may be all the more embracive of chemical activity in this country.

The Executive Committee of the Division of Chemistry and Chemical Technology wish hereby to acknowledge their appreciation of the careful study given to the manuscript by Dr. Clarence J. West and of the verification of all citations by Miss Callie Hull of the Research Information Service of the National Research Council.

Author indexes for Volumes I and II are bound with this volume. They were compiled by Miss Ervye L. Risher, of the Research Information Service. Additional copies of the index for Volume I may be obtained from the publishers.

William J. Hale.

June 30, 1927.

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JULY 1, 1926 TO JULY 1, 1927

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Chapter I.

Theories of Solution.

(July 1, 1925 to July 1, 1927)

Herbert S. Harned,

Professor of Physical Chemistry, University of Pennsylvania

The very important advance made by the theory of Debye and Hückel [1] has been the center of interest in the field of electrolytic solutions during the last few years. This theory of electrolytes rests upon the postulate of complete dissociation of strong electrolytes in dilute or moderately dilute solutions and upon the assumption that it is the inter-ionic attraction which causes the properties of an ionic solution to differ from those of an ideal solute. It is characterized more particularly by the application of the Boltzmann equation and Poisson's equation in order to calculate the distribution of ions of opposite charge around a given ion, the electrical potential of that ion and, subsequently, its free energy. Debye and Hückel's limiting equations for the very dilute solutions based upon the assumption that the ions are electrically charged points appear to be a very close approach to a solution of the problem of very dilute electrolytic solutions and to be well within the errors of the experiments made up to the present time. The most convincing evidence for the validity of their equation for the activity coefficient of an electrolyte in very dilute solution was obtained by Brönsted and LaMer,[2] who measured the solubility of some very slightly soluble higher order cobalt compounds in some salt solutions. Recent work has had to do with the proof of this theory, the possibilities of extending this theory to the more difficult cases of concentrated solutions and to its application to electrolytic solutions containing weak electrolytes.

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[1] Debye and Hückel, *Physik. Z.*, **24**, 185, 305 (1923).

[2] Brönsted and LaMer, *J. Am. Chem. Soc.*, **46**, 555 (1924).

The Limiting Law of the Debye and Hückel Theory. The expression for the activity coefficient, γ, of an electrolyte in very dilute aqueous solution which follows from the theory is

$$\log \gamma = -0.357\, z_1 z_2 \sqrt{2\,\mu} = -0.5\, z_1 z_2 \sqrt{\mu}, \qquad (1)$$

where γ is the activity coefficient of the electrolyte whose ions have the valences z_1 and z_2 and μ is the ionic strength as defined by Lewis and Randall.[3] By measuring the solubility of a tritrivalent salt, namely, $[Co(NH_3)_6]^{III}[Fe(CN)_6]^{III}$, in potassium nitrate solutions, LaMer, King and Mason[4] obtained agreement with equation (1) up to an ionic strength of 0.07 μ. Since $z_1 z_2$ in this case equals 9, the accuracy should be much greater than when a uniunivalent salt is employed. Brönsted and Brumbaugh[5] obtained 0.46 instead of 0.5 for the constant in equation (1) by measuring the solubility of $[Co(NH_3)_6]^{III}[Co(CN)_6]^{III}$ in sodium chloride solutions.

In non-aqueous solutions, the value of the constant in equation (1) differs from 0.357. This according to the theory depends on the dielectric constant of the medium. Thus, in a 50 mol. % ethyl alcohol-water mixture it is 1.105 and in pure alcohol it is 1.973 instead of 0.357. The data of Danner,[6] and Harned and Fleysher[7] on the activity coefficient of hydrochloric acid in alcoholic solutions, examined by Scatchard[8] and by Noyes and Baxter[9] seem to indicate that the results predicted by the theory are well within the experimental error. A similar conclusion has been drawn by Lucasse[10] for hydrochloric acid in glycerol-water mixtures.

Randall and Scott[11] have continued the work of Randall and Vanselow[12] on the freezing point lowerings of dilute aqueous electrolytic solutions. Their measurements of sodium sulfate solutions agree with the Debye and Hückel equation, but their measurements of barium nitrate and sulfuric acid solutions show a disagreement. They interpret this deviation as due to ionic association according to the theory of Bjerrum,[13] or to the formation of undissociated ions in the dilute solutions of these electrolytes. Sodium sulfate they regard as a typical strong electrolyte. Hovorka and Rodebush,[14] from measurements of freezing point lowerings in aqueous solutions of seven electrolytes, found agreement with the limiting equation of the Debye and Hückel theory.

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[3] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921).
[4] LaMer, King, and Mason, *J. Am. Chem. Soc.*, **49**, 363 (1927).
[5] Brönsted and Brumbaugh, *J. Am. Chem. Soc.*, **48**, 2015 (1926).
[6] Danner, *J. Am. Chem. Soc.*, **44**, 2832 (1922).
[7] Harned and Fleysher, *J. Am. Chem. Soc.*, **47**, 82 (1925).
[8] Scatchard, *J. Am. Chem. Soc.*, **47**, 2098 (1925).
[9] Noyes and Baxter, *J. Am. Chem. Soc.*, **47**, 2122 (1925).
[10] Lucasse, *J. Am. Chem. Soc.*, **48**, 626 (1926).
[11] Randall and Scott, *J. Am. Chem. Soc.*, **49**, 647 (1927).
[12] Randall and Vanselow, *J. Am. Chem. Soc.*, **46**, 2418 (1924); *see also* Randall, *J. Am. Chem. Soc.*, **48**, 2512 (1926).
[13] Bjerrum, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **7**, no. 9 (1926).

An interesting study of solutions containing electrolytes of unsymmetrical valence types has been made by LaMer and Mason.[15] They measured the solubility of $[Co(NH_3)_6]^{III}[Co(NH_3)_2(NO_2)_2C_2O_4]^{I}_3$ and $[Co(NH_3)_6]^{III}[Co(NH_3)_2(NO_2)_4]^{I}_3$ in a number of salt solutions of different valence types. When the solvent salt possessed univalent anions, excellent agreement with the Debye and Hückel theory was obtained. When the solvent salt contained polyvalent anions, wide variations from the theoretical equation were obtained even at total concentrations as low as 0.0005 μ. LaMer and Mason think that one cause of the discrepancy is due to neglecting the higher terms of the expansion of a fundamental equation of the Debye and Hückel theory which makes a much greater difference in the cases of the unsymmetrical valence type electrolytes than in the cases of the symmetrical types.

Baxter[16] has found that the activity coefficient of silver iodate at 75° computed from solubility measurements in salt solutions conforms with the limiting equation of the Debye and Hückel theory in the range of ionic strength of from 0.00084 μ to 0.01 μ.

In a mathematical paper, Debye and Pauling[17] proved that any effect which an electrolyte might have on the dielectric constant of the medium would not influence the limiting law of the Debye and Hückel theory.

Adams[18] contends that the virial term for the energy of strong electrolytes derived from the dielectric constant of water should be denoted ΔF (free energy at constant pressure), not ΔU (total internal energy). If this is the case, these two quantities are only equal when the dielectric constant is independent of the temperature.

Concentrated Solutions. When we proceed from the ideal conditions where the ions are taken to be charged points without size to conditions where the ionic diameters must be taken into account, the interpretation of the behavior of an electrolytic solution becomes much more difficult. We have to consider the possibilities of ionic association, of the change in the dielectric constant with the change in concentration of the electrolyte, of the influence of ionic hydration, etc. Since, up to the present time, our measurements give only the result of such combined influences and do not permit the study of them separately, we cannot expect convincing proof of the theoretical assumptions or the mathematical methods of treatment.

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[14] Hovorka and Rodebush, *J. Am. Chem. Soc.*, 47, 1614 (1925); Rodebush, *J. Am. Chem. Soc.*, 48, 709 (1926).

[15] LaMer and Mason, *J. Am. Chem. Soc.*, 49, 410 (1927).

[16] Baxter, *J. Am. Chem. Soc.*, 48, 615 (1926).

[17] Debye and Pauling, *J. Am. Chem. Soc.*, 47, 2129 (1925).

[18] Adams, *J. Am. Chem. Soc.*, 48, 621 (1926).

A convenient method of systematizing this review is to consider the equation for the activity coefficient of a single electrolyte derived by Hückel [19] from the extended theory of Debye and Hückel. This equation is

$$\log \gamma = -\frac{u\sqrt{2\,\mu}}{1 + A\sqrt{2\,\mu}} + B(2\,\mu) - \log\left(1 + \frac{M_0}{1000}\,\nu m\right), \qquad (2)$$

where u is the theoretical constant of the limiting law of the theory, A is a constant which depends on the mean distance of approach of the ions, and B is a constant which depends on the dielectric constant of the medium and which is characteristic of the ions which the solution contains. The third term on the right of this equation has no theoretical significance but is merely employed to change $\log f$, where f is the activity divided by the mol fraction, to $\log \gamma$ where γ is the activity divided by the molality, M_0 is the molal weight of solvent and m is the molality of the electrolyte. This equation neglects the possibility of ionic association.

In the last two years considerable data from electromotive force measurements in concentrated solutions have been obtained by American investigators. Harned and Fleysher [7] have determined hydrochloric acid in water-alcohol mixtures. Scatchard [20] has determined hydrochloric acid in aqueous solution and aqueous solutions containing sucrose and Lucasse [10] has determined hydrochloric acid in glycerol-water mixtures. Harned [21] has determined hydrochloric acid in univalent and bivalent chloride solutions and Randall and Breckenridge [22] have measured it in barium and lanthanum chloride solutions. Calcium, strontium, and barium chlorides have been measured by Lucasse,[23] barium chloride by Pearce and Gelbach,[24] barium bromide by Gelbach and Huppke,[25] the alkali metal sulfates by Åkerlöf [26] and potassium and sodium bromides and iodides by Harned and Douglas.[27] Sodium and lithium hydroxides have been studied by Harned [28] and Harned and Swindells.[29] Livingston [30] has measured hydrobromic acid in aqueous solution. The activity coefficient of sulfuric acid in sulfate solutions has been determined by Harned and Sturgis,[31] Åkerlöf [26] and Randall and Langford.[32] Hydrobromic acid in sulfate solutions has been determined by Livingston [30] and in bromide solutions by Harned and James.[33] Potassium, sodium and lithium hydroxides in chloride and bromide solutions have been investigated by Harned,[34] Harned and Swindells [29] and Harned and James [33] and in sulfate solutions by Åkerlöf.[26]

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[19] Hückel, *Physik. Z.*, **26**, 93 (1925).
[20] Scatchard, *J. Am. Chem. Soc.*, **47**, 641 (1925); **48**, 2026 (1926).
[21] Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).
[22] Randall and Breckenridge, *J. Am. Chem. Soc.*, **49**, 1435 (1927).
[23] Lucasse, *J. Am. Chem. Soc.*, **47**, 743 (1925).

Equation (2) has been shown to satisfy the results for a single electrolyte in aqueous or non-aqueous solutions by Hückel,[19] Scatchard,[8] Lucasse,[35] Harned,[21] Harned and Åkerlöf [36] and Harned and Douglas [27] as long as the A and B constants are taken arbitrarily. This does not confirm the theory but only the approximate formal validity of the equation. Thus, in many cases the values of A are of the correct order of magnitude, but the values of B are such that in some cases (*e.g.*, HCl,LiCl) the dielectric constant would be zero at 4*M* salt concentration, an obvious impossibility. Further, for sodium and lithium hydroxides, the A values are smaller than would be expected.

Equation (2) in the form

$$\log \gamma = -\frac{u\sqrt{2\,\mu_T}}{1 + \mathrm{A}\sqrt{2\,\mu_T}} + \mathrm{B}(2\,\mu_1) + \mathrm{B}'(2\,\mu_T - 2\,\mu_1) - \log\left(1 + \frac{Mu}{1000}\,\nu m_1\right) \qquad (3)$$

has been shown by Harned [21] and by Harned and Åkerlöf [36] to be valid for the activity coefficients of hydrochloric acid, sulfuric acid and potassium, sodium and lithium hydroxides in salt solutions if the constants A, B and B′ be varied arbitrarily. B′ is an additional constant required for the calculation of mixtures. μ_1 is the ionic strength of the electrolyte whose activity coefficient is γ, μ_T is the total ionic strength. Further, Harned [21] showed that the activity coefficient of hydrochloric acid in salt solutions may be calculated from the data of the single electrolytes from Hückel's equations. This agreement is to be regarded as formal. Indeed, no such calculation can be made for the hydroxides and the hydroxide-salt mixtures as pointed out by Harned and Åkerlöf.[36]

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[24] Pearce and Gelbach, *J. Phys. Chem.*, **29**, 1023 (1925).

[25] Gelbach and Huppke, *J. Am. Chem. Soc.*, **48**, 1504 (1926).

[26] Åkerlöf, *J. Am. Chem. Soc.*, **48**, 1160 (1926).

[27] Harned and Douglas, *J. Am. Chem. Soc.*, **48**, 3095 (1926).

[28] Harned, *J. Am. Chem. Soc.*, **47**, 676 (1925).

[29] Harned and Swindells, *J. Am. Chem. Soc.*, **48**, 126 (1926).

[30] Livingston, *J. Am. Chem. Soc.*, **48**, 45 (1926).

[31] Harned and Sturgis, *J. Am. Chem. Soc.*, **47**, 945 (1925).

[32] Randall and Langford, *J. Am. Chem. Soc.*, **49**, 1445 (1927).

[33] Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

[34] Harned, *J. Am. Chem. Soc.*, **47**, 684, 689 (1925).

[35] Lucasse, *Z. physik. Chem.*, **121**, 254 (1926).

[36] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

For mixtures of uniunivalent electrolytes at constant total molality, equation (3) reduces to the simple form of

$$\log \gamma = am + \text{constant} \qquad (4)$$

where a is a constant. Thus the log γ is a linear function of the concentration of the electrolyte whose concentration is m. This law has been shown by Harned [21] to be valid even in solutions of $3M$ total concentration for hydrochloric acid in uniunivalent chloride solutions. Indeed, the linear term in equations (2) and (3) seems to be the most important characteristic of the behavior of all these concentrated solutions.[37]

Remarks Concerning the Theory of Electrolytes. The limiting law obtained from the theory of Debye and Hückel has been found to be valid within the error of experiment for all cases of simple strong electrolytes. This represents a very important advance, and it seems probable that it will be a long time before a more exact expression will be derived.

When we consider moderately concentrated and concentrated solutions, the whole situation becomes obscure. The extended theory of Debye and Hückel gives probable values for "the mean ionic distances" in some cases and improbable values in others. Perhaps this is to be explained by ionic association in a manner postulated by Bjerrum, but even then it is very difficult to separate the influence on the potential of an ion due to its size and the size of the other ions from the effect of association, the effect of the possible variation of the dielectric constant, and the effect of hydration. The values derived for the constants in equations (3) and (4) must be regarded as partially formal and at their best only rough expressions for what is actually taking place.

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[37] *See also* Güntelberg, *Z. physik. Chem.*, **123**, **199** **(1926)**.

Applications to Weak Electrolytes. Sherrill and Noyes[38] and independently MacInnes[39] have employed the conclusions of the Debye and Hückel theory for the calculation of the dissociation constants of moderately strong and weak electrolytes. They have employed the equation

$$K = \frac{\alpha\gamma_{H^+}\alpha\gamma_{A^-}C}{(1-\alpha)\gamma_{HA}} \tag{5}$$

where γ_{H^+}, γ_{A^-}, and γ_{HA} are the activity coefficients of the species denoted by subscripts and α is the degree of dissociation calculated from conductances by a method which takes into account the variation of the ionic mobilities with the concentration. Sherrill and Noyes obtained excellent agreement for the first dissociations of phosphoric and sulfurous acids and the second dissociation of sulfuric acid. MacInnes found good concordance in the cases of acetic, *o*-chlorobenzoic, 3, 5-dinitrobenzoic, cyanoacetic and *o*-nitrobenzoic acids.

The thermodynamic equilibrium constant for an ionic dissociation of a weak uniunivalent electrolyte is given by

$$K = \frac{a_C a_A}{a_{CA}} = \frac{\gamma_C\gamma_A}{\gamma_{CA}}\,\frac{c_C c_A}{c_{CA}} \tag{6}$$

where the "*a*," the "*γ*" and the "*c*" are the activities, activity coefficients and concentrations of the species denoted by subscripts. Upon the addition of a salt, $\gamma_C\gamma_A$ is changed and therefore $c_C c_A$ changes with the ionic strength of the solution. Thus, if $\frac{\gamma_C\gamma_A}{\gamma_{CA}}$ can be determined, $\frac{c_C c_A}{c_{CA}}$ can be computed or *vice versa*. In dilute solutions, where γ_{CA} equals unity and $\gamma_C\gamma_A$ can be calculated by the Debye and Hückel theory, $\frac{c_C c_A}{c_{CA}}$ will be known. This effect in its relation to hydrogen and hydroxyl ion catalysis has been studied by Brönsted and King,[40] Kilpatrick,[41] and Harned.[42]

Electromotive force measurements have been employed for determining the quantity $\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$ or the ionic activity coefficient product of water in salt solutions. From these data, from the known dissociation constant of water and by means of equation (6), the dissociation of water in chloride, bromide and sulfate solutions has been determined by Harned,[43] Harned and Swindells,[29] Åkerlöf [26] and Harned and James.[33]

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[38] Sherrill and Noyes, *J. Am. Chem. Soc.*, 48, 1861 (1926).
[39] MacInnes, *J. Am. Chem. Soc.*, 48, 2068 (1926).
[40] Brönsted and King, *J. Am. Chem. Soc.*, 47, 2523 (1925).
[41] Kilpatrick, *J. Am. Chem. Soc.*, 48, 2091 (1926).
[42] Harned, *J. Am. Chem. Soc.*, 49, 1 (1927).

A very thorough experimental investigation of the activity coefficients of the ions in phosphate solutions from electromotive force measurements has been made by Cohn.[44] An accurate investigation of the solubilities and electromotive forces of the alkali carbonates by Walker, Bray and Johnston [45] has increased our knowledge of the equilibria in carbonate solutions to a considerable extent. Randall, McBain and White [46] have studied the activity coefficients of soap solutions.

Hydration of Ions. Webb [47] has contributed an excellent investigation on the free energies of hydration of the ions. The free energy of hydration of an ion "is obtained by calculating the energy necessary to charge the ion in a vacuum and that necessary to charge the ion in water and compress the solvent in the vicinity of the ion." To do this, Langevin's theory [48] of dielectric constants as applied by Debye [49] was employed. The free energies of hydration and subsequently the electron affinities and lattice energies of a number of the simple ions were calculated.

Liquid Junction Potentials. Harned [50] has made an analysis of the general thermodynamic equation for liquid junction potentials and has shown why and to what extent Henderson's equation must be modified in order to be exact. The relation of liquid junction potential to individual ion activity coefficient has also been investigated and the definitions and postulates necessary to fix the liquid junction potential have been discussed.

Transference Numbers. MacInnes and Brighton [51] and Smith and MacInnes [52] have continued the investigation of MacInnes and Smith [53] on the moving boundary method for determining transference numbers. By improving the method of making the contact between the indicator solution and the salt solution, they have greatly increased the accuracy of their measurements. MacInnes, Cowperthwaite and Blanchard[54] have devised a photo-electric relay system which maintains a constant current through the moving boundary apparatus. Considerations of MacInnes[55] and measurements of Dewey[56] indicate that no complexes of the form $K_x(NaCl_2)_y$ exist in the moderately dilute solutions of mixtures of simple ions as previously predicted by Schneider and Braley.[57] The same conclusion was drawn by Taylor.[58]

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[43] Harned, *J. Am. Chem. Soc.*, **47**, 930 (1925).

[44] Cohn, *J. Am. Chem. Soc.*, **49**, 173 (1927).

[45] Walker, Bray and Johnston, *J. Am. Chem. Soc.*, **49**, 1235 (1927).

[46] Randall, McBain and White, *J. Am. Chem. Soc.*, **48**, 2517 (1926).

[47] Webb, *J. Am. Chem. Soc.*, **48**, 2589 (1926).

[48] Langevin, *J. de phys.*, (4) **4**, 678 (1905); *Ann. chim. phys.*, (8) **5**, 70 (1905).

[49] Debye, "Marx' Handbuch der Radiologie," **6**, 618, 680. Leipzig, Akademische Verlagsgesellschaft, 1925.

[50] Harned, *J. Phys. Chem.*, **30**, 433 (1926).

[51] MacInnes and Brighton, *J. Am. Chem. Soc.*, **47**, 994 (1925).

[52] Smith and MacInnes, *J. Am. Chem. Soc.*, **47**, 1009 (1925).

[53] MacInnes and Smith, *J. Am. Chem. Soc.*, **45**, 2246 (1923); Smith and MacInnes, *J. Am. Chem. Soc.*, **46**, 1398 (1924).

Transference numbers of hydrochloric acid in alcohol and alcohol-water mixtures from electromotive force data have been obtained by Harned and Fleysher,[7] and in glycerol-water mixtures by Lucasse.[59] Lucasse[23] has also determined the transference numbers of the alkaline earth halides.

Conductances of Electrolytic Solutions. Ruby and Kawai[60] have studied the densities, equivalent conductances and viscosities of some solutions of halides and their mixtures. Randall and Scalione[61] have measured the conductances of dilute aqueous solutions of the alkali metals hydroxides. This latter investigation supplies some much needed data on this subject since no accurate data at 25° had previously been obtained. Randall and Scott[62] have also measured the conductances of aqueous solutions of barium nitrate, sodium sulfate and sulfuric acid at 0°.

Activities and Homogeneous Catalysis. The investigation of Livingston[63] on the catalytic decomposition of hydrogen peroxide in hydrobromic acid-bromide solutions has shown that the velocity constant of the reaction is proportional to the activity product of the hydrogen and bromide ions. Åkerlöf,[64] from measurements of the hydroxyl ion catalysis of the decomposition of diacetone alcohol in salt solutions, has concluded that the velocity constant of this reaction parallels but is not proportional to the activity of the hydroxyl ion. Taylor and Close,[65] as a result of a study of the hydrogen ion catalysis of lactone formation, conclude that the velocity constant is a function of the activity of the hydrogen ion.

[54] MacInnes, Cowperthwaite, and Blanchard, *J. Am. Chem. Soc.*, **48**, 1909 (1926).
[55] MacInnes, *J. Am. Chem. Soc.*, **47**, 1922 (1925).
[56] Dewey, *J. Am. Chem. Soc.*, **47**, 1927 (1925).
[57] Schneider and Braley, *J. Am. Chem. Soc.*, **45**, 1121 (1923); *cf.* Braley and Rippie, *ibid.*, **49**, 1493 (1927).
[58] Taylor, *J. Am. Chem. Soc.*, **48**, 599 (1926).
[59] Lucasse, *J. Phys. Chem.*, **30**, 562 (1926).
[60] Ruby and Kawai, *J. Am. Chem. Soc.*, **48**, 1119 (1926).
[61] Randall and Scalione, *J. Am. Chem. Soc.*, **49**, 1486 (1927).
[62] Randall and Scott, *J. Am. Chem. Soc.*, **49**, 636, 647 (1927).
[63] Livingston, *J. Am. Chem. Soc.*, **48**, 53 (1926).
[64] Åkerlöf, *J. Am. Chem. Soc.*, **48**, 3046 (1926).
[65] Taylor and Close, *J. Phys. Chem.*, **29**, 1085 (1925).

Chapter II.

Gases and Gas Mixtures.* †

(July 1, 1925 to July 1, 1927)

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The past half dozen years or more has been a period during which a renewed interest has been evident in the experimental and theoretical study of the properties of gases. In this connection it is of interest to recall that almost exactly a hundred years ago the question of the limitations of Boyle's or Mariotte's law, Gay-Lussac or Charles' law relative to the p-v-T properties began to receive serious attention.[1] The measurements of Despretz, in fact, demonstrated that even a little above one atmosphere such gases as ammonia, hydrogen sulfide, and cyanogen exhibited a more rapid diminution in volume than called for by Boyle's law. Despretz's manipulative skill is indeed well demonstrated by the fact that he found Boyle's law invalid for air above twenty atmospheres.

Aside from the p-v-T properties of gases, in recent years the dielectric constants, magnetic characteristics, refractive indices, light scattering properties, viscosities, interdiffusion coefficients, and absorption spectra are being investigated. These data will provide in time sufficient material for understanding in much detail the nature and properties of the intermolecular field of force upon which the p-v-T properties of substances in all states of aggregation depend. Many indications bearing on the nature of chemical binding forces, the theory of reaction rates, and mass law effects, among other important problems, will be forthcoming from these investigations. The technique for the precise measurement of all these properties is developing rapidly and the next few years will undoubtedly witness a more general appreciation of their importance, to chemistry in particular.

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* The present report will be concerned almost entirely with the compressibility of gases and their mixtures in the homogeneous phase.

† Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, Cambridge, No. 203.

[1] Orsted and Suensson, *Edin. J. Sci.*, **4**, 224 (1826). Despretz, *Ann. chim. phys.*, **34**, 335 (1827).

Compressibilities of Pure Gases. The American contribution to the experimental determination of compressibilities has been considerable during the period covered by this report. The experimental technique developed has been varied and the widest possible diversification in the methods of measurement is highly desirable. The measurements reported have been carried out at the Fixed Nitrogen Research Laboratory, Washington, Harvard University, and the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology. The National Bureau of Standards has in the past contributed valuable data and experimental methods but no new data have appeared between July, 1925 and July, 1927.

The investigations at low pressures are conveniently considered apart from those at higher pressures. New precise investigations of the volumes of various masses of nitrogen and oxygen between one atmosphere and one-quarter atmosphere have been reported by Baxter and Starkweather.[2] These investigators give for the volumes of a gram of helium at 0° 5603.5 cc. At lower pressures the density measurements indicated no departure from Boyle's law. The compressibilities of helium at higher pressures indicate,[3] on extrapolation to zero pressure, that the ratio of pv at one atmosphere to that at zero pressure is about 1.00053.

The volumes of one gram of nitrogen are: at one atmosphere and 0° 799.77 cc.; at 0.666671 atmosphere 1199.79 cc.; and at 0.333329 atmosphere 2399.98 cc. With the pv product at one atmosphere taken as unity, the pv products in this range of pressure are given by $pv = 1.00040 - 0.0004\ p^{\text{atm.}}$ Similar data for oxygen are: at one atmosphere and 0° 699.81 cc.; at 0.75 atmosphere 1071.49 cc.; at 0.5 atmosphere 1400.286 cc.; and at 0.25 atmosphere 2801.20 cc. These data lead to a mean molecular weight of N_2, 14.007.

The isothermal compressibilities of hydrogen and nitrogen have been reinvestigated to 1000 atmospheres at 0° by Bartlett.[4] The results obtained agree closely with the results obtained for atmospheric nitrogen by Amagat. In the case of hydrogen, however, Bartlett obtained values for the pressure-volume products which are uniformly lower than the Amagat data. The new data to 200 atmospheres are in good agreement with the reported results of other observers. Data for both these gases are of great importance in chemical syntheses and there is great need of extending the measurements to high temperatures although the difficulties increase tremendously above 100°. The data are of course fundamentally important in connection with the development of the equation of state problem upon which, in large measure, the generalized treatment of nonperfect gas chemical equilibria depends. Attention may be called to a correction published by Smith and Taylor[5] relative to their investigation of pure nitrogen between 0 and 200°.

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[2] Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, **12**, 20, 703 (1926).
[3] Bureau of Standards, Circular No. 279 (1926).
[4] Bartlett, *J. Am. Chem. Soc.*, **49**, 687 (1927).

A recent review[6] of all available data for pure nitrogen discloses the fact that no two observers agree within better than 0.1% in their reported values of the pv products over the temperature range 0 to 200°.

Mixtures of Gases. Gaseous mixtures have not been systematically investigated, although recently Bartlett[4] has measured the compressibility of eight nitrogen-hydrogen mixtures at 0 to 1000 atmospheres. The correlation of the data was accomplished by expressing the constants of the formula

$$(pv) = \mathrm{A} + \mathrm{B}p + \mathrm{C}p^2 + \mathrm{D}p^3$$

for the mixtures as functions of the composition of form, for example,

$$\mathrm{B} = \mathrm{a} + \mathrm{b}x + \mathrm{c}x^2 + \mathrm{d}x^3$$

where x is the mole % of nitrogen in the mixture. In the range of pressure 350 to 1000 atmospheres, it is possible to represent the data to 0.27% by the correlation method used, neglecting x^3. Below 350 atmospheres all terms of the expression for x given must be employed. The simplification above 350 atmospheres is due to the fact that the pv products become, above this pressure, nearly linear functions of the pressure.

Reference may be made also to the dissertation of Burks[7] wherein two mixtures of nitrogen-methane were measured at 0,

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[5] Smith and Taylor, *J. Am. Chem. Soc.*, 48, 3122 (1926).

[6] Keyes and Taylor, *J. Am. Chem. Soc.*, 49, 896 (1927).

[7] H. G. Burks, *Thesis*, *M. I. T.*, 1925.

50, 100, 150 and 200 atmospheres by a constant volume method for volumes from 40 cc. per gram to 10 cc. per gram. These isometrics show slight curvature which, however, diminishes at the higher temperatures. The data were found capable of a tolerably satisfactory correlation, for purposes of computing the pressures, by means of the equation of state of Keyes.[8] An examination of the constants of the equation of state for the mixtures together with those of pure methane[9] and nitrogen determined in the same apparatus indicated that the constants for the mixture were linear functions of the composition and constants for the pure gases, except the cohesive pressure constant A. The square root of the latter constant appears to be a linear function of the composition and constants of the separate gases

$$[\textit{i.e.,}\ \sqrt{A}_{\text{mix.}} = (\sqrt{A}_{CH_4} n_{CH_4} + \sqrt{A}_{N_2} n_{N_2})].$$

Special Mixtures. The importance of investigating the effect of an indifferent gas on a univarient system as regards the variation in content of the gaseous component of the univarient equilibrium in the gaseous phase appears to have been pointed out first by Gillespie.[10] The solid phases form in this case the equivalent of a semi-permeable membrane and (neglecting the solubility of the indifferent gas in the solid phase) the equilibrium pressure of the gaseous phase of the univarient system is fixed at constant temperature regardless of how great the pressure of the indifferent gas (assuming the solid phases to be incompressible). Lurie and Gillespie[11] have published measurements in which the univarient system was $BaCl_2 \cdot 8\,NH_3 + BaCl_2$ and the indifferent gas nitrogen. It was found that the amount of ammonia in the gaseous phase increased more rapidly than would be expected by Dalton's rule of partial pressures. The data were correlated by the use of the modified fugacity rule due to Gillespie.

Several recent investigations have been published reporting the compositions of the gaseous phase when an indifferent gas is used to compress a liquid. Thus, Larson and Black[12] made an extensive investigation of the system ammonia-hydrogen-nitrogen at pressures to 1000 atmospheres and recently Bartlett[13] has published measurements for the system water-nitrogen, water-hydrogen, and water-(nitrogen-hydrogen) mixtures.

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[8] Keyes, *Proc. Nat. Acad. Sci.*, 3, 323 (1917).
[9] Keyes and Burks, *J. Am. Chem. Soc.*. 49, 1403 (1927).
[10] Gillespie, *J. Am. Chem. Soc.*, 47, 305 (1925).
[11] Lurie and Gillespie, *J. Am. Chem. Soc.*, 49, 1146 (1927).
[12] Larson and Black, *J. Am. Chem. Soc.*, 47, 1015 (1925).
[13] Bartlett, *J. Am. Chem. Soc.*, 49, 65 (1927).

Every case examined discloses the fact that a greater amount of the vapor phase of the liquid is present in the homogeneous gas phase composition than is accounted for from Dalton's additive pressure rule. The magnitude of the effect (the effect is sometimes referred to as a "solubility effect") depends upon the nature of the indifferent gas. Thus in the water-hydrogen and water-nitrogen mixtures used by Bartlett the latter mixture at 1000 atmospheres and 50° contained more water vapor (44%) than the water-hydrogen system under the same conditions.

The correlation of the results of the liquid-gas systems referred to is a difficult matter, although Lurie and Gillespie [11] have succeeded in correlating the data tolerably well in the case of carbon dioxide-nitrogen using a treatment similar to that employed for the barium chloride ammine-nitrogen system. A variety of supplementary data will be required before it will be possible to proceed quantitatively in correlating the data for the liquid-gas systems but the theoretical foundation has been laid and the continued accumulation of the necessary data will provide material whereby the numerical methods of treatment may be improved.

Further Investigations

This report has included substantially investigations related directly to pressure-volume-temperature properties. It is evident that convenient use of the available data depends largely on a knowledge of the rational equation of state for pure gases as well as mixtures. Moreover as the form of the equation of state becomes better known, a smaller amount of experimental data will be required to determine the constants of the equation of state. A very important part of the investigations relating to p-v-T properties can be profitably directed to selecting substances and ranges of the variables involved which will be favorable for use in equation of state investigations.

Further measurements should also be made on gaseous equilibria where the pressures are as high as possible, in order that theories of non-perfect gaseous equilibria may be tested. The following list of investigations gives illustrations of what is believed is more immediately needed to favor the development of a more generalized thermodynamic treatment of chemical and physico-chemical problems.

1. The experimental determination, to as high temperatures as possible (500°), of the p-v products for helium, hydrogen, neon, argon and nitrogen. The difficulties are tremendous because of the difficulty of finding a suitable container, and when the container is found, of determining the physical properties of the container for use in correcting for temperature dilation and stretch under pressure.

2. An investigation of the isometrics of noble gas mixtures; probably

argon and neon are best suited. The temperature range should be from 100 to 200°.

3. An investigation of a ternary mixture. Since CH_4-N_2 has been investigated and for other reasons (non-reactivity values of the equation of state constants) one or two mixtures as, for example, (CH_4-N_2-CO_2) or (CH_4-N_2-C_2H_6) would be very suitable.

4. An investigation of the "polar type" substances [(index of refraction)^2 dielectric constant], sulfur dioxide, methyl alcohol, ethyl alcohol, and methylamine. Gases which are attacked by mercury are difficult to deal with and may be excluded in favor of substances of similar properties which do not attack mercury.

5. A binary mixture of two "polar type" gases should be completed. Ammonia and methylamine would be excellent, especially since very complete data for pure ammonia will soon be published.

Chapter III.

Phase Equilibrium Data.

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The material comprised within the topic of heterogeneous equilibrium is itself so heterogeneous that a survey of it, within the allotted space, can be little more than a catalog; moreover, even if we exclude from our list those papers which would clearly be treated under one of the other headings in this volume (*e.g.*, metals, earth metal oxides), the papers included within this category, published during the last two years, number nearly two hundred. From this it is obvious that every paper cannot be mentioned, far less discussed, even were it desirable with respect to the reader's interest to do so. I have attempted therefore merely to indicate the main lines of work, and take them up for convenience in the order of the number of components involved. The reader desiring a systematic discussion of what is, from the practical point of view, a very important part of the general topic will find it in Blasdale's "Equilibria in Saturated Salt Solutions." [1]

One Component Systems. There have been quite a number of papers dealing with the vapor pressure of pure substances, a large proportion of the measurements having been carried out with some further purpose in view. From the University of Illinois have come [2] what are probably the best single series of determinations now available of the vapor pressure of the metals zinc, lead, sodium and potassium, and also of the five alkali halides. At a much lower region on the temperature scale there are papers from the cryogenic laboratory of the U. S. Bureau of Mines[3] dealing with the vapor pressure of nitrogen; of cyanogen and hydrocyanic acid, both as solid and liquid, and of ethane; that of nitrogen and oxygen, and also of carbon dioxide, has also been measured.[4] There have been studies of the vapor pressure of compounds of possible importance (a) in the manufacture of dyes in the U. S. Bureau of Chemistry,[5] (b) in the manufacture of explosives in the U. S. Bureau of Mines.[6] From Cornell[7] have appeared papers on germanium compounds. In addition data have been published on various hydrocarbons,[8] gasolene[9] (which is, of course, hardly a one-component system), acetone[10] and other solvents,[11] phosgene[12] and sulfur monochloride.[13]

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* I wish to acknowledge my indebtedness to Dr. Laura Cannon and to Dr. Florence Fenwick, who were good enough to search and collate the literature for me.

[1] Blasdale, "Equilibria in Saturated Salt Solutions," New York, Chem. Catalog Co., 1927, 197 p.

[2] Rodebush and Dixon, *J. Am. Chem. Soc.*, 47, 1036 (1925); Rodebush and DeVries, *J. Am. Chem. Soc.*, 47, 2488 (1925); Fiock and Rodebush, *J. Am. Chem. Soc.*, 48, 2522 (1926).

With respect to the vapor pressure of solids, there are data on naphthalene and some disubstituted benzenes,[14] some substituted quinones,[15] oxalic acid[16] and benzoic acid[16a]; also on arsenic trioxide,[17] for which the regions of stability of the several forms were mapped out.

Turning now specifically to the equilibrium between condensed phases, we find an investigation of two metastable forms of ammonium nitrate,[18] which transform more rapidly and dependably than is the case with most transformations of stable crystal forms. In this connection it may be remarked that there is room for much research to secure information as to the relation (if there be any) between ease of transformation, change of volume and of heat content, and the basic crystal structure of the forms involved.

[3] Porter and Perry, *J. Am. Chem. Soc.*, **48**, 2059 (1926); Perry and Bardwell, *J. Am. Chem. Soc.*, **47**, 2629 (1925); Perry and Porter, *J. Am. Chem. Soc.*, **48**, 299 (1926); Loomis and Walters, *J. Am. Chem. Soc.*, **48**, 2051 (1926); Porter, *J. Am. Chem. Soc.*, **48**, 2055 (1926).

[4] Dodge and Davis, *J. Am. Chem. Soc.*, **49**, 610 (1927); Dodge and Dunbar, *J. Am. Chem. Soc.*, **49**, 591 (1927); Bridgeman, *J. Am. Chem. Soc.*, **49**, 1174 (1927).

[5] Nelson and Wales, *J. Am. Chem. Soc.*, **47**, 867 (1925); Berliner and May, *J. Am. Chem. Soc.*, **47**, 2350 (1925); **48**, 2630 (1926); **49**, 1007 (1927); May, Berliner and Lynch, *J. Am. Chem. Soc.*, **49**, 1012 (1927).

[6] Rinkenbach, *Ind. Eng. Chem.*, **18**, 1195 (1926); Taylor and Rinkenbach, *Ind. Eng. Chem.*, **18**, 676 (1926); *J. Am. Chem. Soc.*, **48**, 1305 (1926).

[7] Corey, Laubengayer, and Dennis, *J. Am. Chem. Soc.*, **47**, 112 (1925); Laubengayer and Tabern, *J. Phys. Chem.*, **30**, 1047 (1926); Dennis, Orndorff and Tabern, *J. Phys. Chem.*, **30**, 1049 (1926); Dennis and Hance, *J. Phys. Chem.*, **30**, 1055 (1926).

[8] Leslie and Carr, *Ind. Eng. Chem.*, **17**, 810 (1925).

[9] Stevenson and Stark, *Ind. Eng. Chem.*, **17**, 679 (1925); Davis, *Ind. Eng. Chem.*, **17**, 1136 (1925).

[10] Felsing and Durban, *J. Am. Chem. Soc.*, **48**, 2885 (1926).

[11] Davidson, *Ind. Eng. Chem.*, **18**, 669 (1926).

[12] Germann and Taylor, *J. Am. Chem. Soc.*, **48**, 1154 (1926).

[13] Harvey and Schuette, *J. Am. Chem. Soc.*, **48**, 2065 (1926).

[14] Andrews, *J. Phys. Chem.*, **30**, 1497 (1926); Swan and Mack, *J. Am. Chem. Soc.*, **47**, 2112 (1925).

[15] Coolidge and Coolidge, *J. Am. Chem. Soc.*, **49**, 100 (1927).

[16] Noyes, Wobbe and Flanigan, *J. Am. Chem. Soc.*, **48**, 1882 (1926).

[16a] Klosky and Woo, *J. Am. Chem. Soc.*, **49**, 1280 (1927).

[17] Rushton and Daniels, *J. Am. Chem. Soc.*, **48**, 384 (1926).

[18] Bowen, *J. Phys. Chem.*, **30**, 721 (1926).

There is also an almost complete lack of knowledge of the factors which determine the crystallization of a form which is under the conditions thermodynamically unstable (*e.g.*, calcite, aragonite); any positive definite information in this direction would be very valuable. Papers along a line not unrelated to this, dealing namely with thermal data on organic compounds, have appeared from Stanford [19] and from Yale.[20] This leads to the remark that, for *pure* organic substances, even the melting temperature is not generally known with the accuracy which an ingenuous person would suppose it to have from the number of significant figures used to express it.

Two-Component Systems. Frazer and his collaborators,[21] in continuation of their very accurate work on the vapor pressure of aqueous solutions, have published results on solutions of potassium nitrate and of sulfuric acid; coordinate in accuracy with these are freezing point depressions of dilute solutions of various salts.[22] The vapor pressure of aqueous solutions of glycerol, glycerol-sodium chloride, bromine and phenol have also been investigated in connection with the design of evaporators and stills [23]; the freezing and solubility curves of orthophosphoric acid have been fixed [24] and the phase relations in the system lithium chlorate-water have been investigated.[24a] On non-aqueous liquid systems there are vapor pressure data on lithium-ammonia,[25] mixtures of alcohols [26] and of hydrocarbons,[26a] on some systems containing phosgene [27] and on carbon dioxide-acetone.[10]

A welcome addition to the scanty knowledge of the equilibrium between hydrocarbons and hydrogen is afforded by a paper [28] on the system benzene-cyclohexane-hydrogen. A number of cases of the equilibrium solids-gas have been studied; these include the decomposition of sodium carbide,[29] the reduction of nickel oxide by hydrogen,[30] of zirconia by carbon [31] and of zinc oxide by carbon monoxide.[32] The last is of considerable metallurgical importance, as it at last provides a basis upon which to build up a more efficient process of producing zinc than has been possible hitherto by direct reduction. A reinvestigation of the palladium-hydrogen system [33] indicates that there are two solid solutions; the occurrence of solid solution in other metal systems is dealt with under another heading.

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[19] Parks, *J. Am. Chem. Soc.*, 47, 338 (1925); Parks and Huffman, *J. Am. Chem. Soc.*, 48, 2788 (1926).

[20] Andrews, Lynn and Johnston, *J. Am. Chem. Soc.*, 48, 1274 (1926).

[21] Frazer, Lovelace and Taylor, *J. Phys. Chem.*, 30, 1669 (1926); Grollman and Frazer, *J. Am. Chem. Soc.*, 47, 712 (1925).

[22] Hovorka and Rodebush, *J. Am. Chem. Soc.*, 47, 1614 (1925); Randall and Scott, *J. Am. Chem. Soc.*, 49, 647 (1927).

[23] Carr, Townsend and Badger, *Ind. Eng. Chem.*, 17, 643 (1925); Rhodes, Wells and Murray, *Ind. Eng. Chem.*, 17, 1199 (1925); Rhodes and Bascom, *Ind. Eng. Chem.*, 19, 480 (1927).

[24] Ross and Jones, *J. Am. Chem. Soc.*, 47, 2165 (1925).

[24a] Kraus and Burgess, *J. Am. Chem. Soc.*, 49, 1226 (1927).

[25] Kraus and Johnson, *J. Am. Chem. Soc.*, 47, 725 (1925).

[26] Parks and Kelley, *J. Phys. Chem.*, 29, 727 (1925).

[26a] Calingaert and Hitchcock, *J. Am. Chem. Soc.*, 49, 750 (1927).

[27] Germann and McIntyre, *J. Phys. Chem.*, 29, 102 (1925); Germann and Timpany, *J. Phys. Chem.*, 29, 1423 (1925); Germann and Birosel, *J. Phys. Chem.*, 29, 1469 (1925).

[28] Burrows and Lucarini, *J. Am. Chem. Soc.*, 49, 1157 (1927).

To return now to aqueous solutions, there are mutual solubility data on phenol, butyl alcohol [34] and certain ethers,[35] the last named exhibiting completely closed solubility curves; and solubility determinations of a number of salts, including salts of several of the rare earths, in part apparently undertaken in connection with the development of analytical methods.[36] For this specific reason the solubility of the alkali perchlorates in mixtures of common alcohols was measured.[37] The equilibrium between copper, Cu^+ and Cu^{++}, was determined electrometrically,[38] this being the only example of this type of system published in America during the last two years.

There have been a number of solubility investigations undertaken primarily to secure information of a type which might enable one more accurately to predict the solubility in a particular system than is now feasible. As examples, there are data on the solubility in a series of solvents over a considerable temperature range of naphthalene; [39] stannic iodide; [40] the three isomeric nitroanilines,[41] which yield curves in general very similar, yet showing incomplete parallelism; further on the reciprocal solubility of the triads of the chloronitrobenzenes, nitroanilines and dinitroben-

[29] Guernsey and Sherman, *J. Am. Chem. Soc.*, **48**, 140 (1926).

[30] Prescott, *J. Am. Chem. Soc.*, **48**, 2534 (1926).

[31] Pease and Cook, *J. Am. Chem. Soc.*, **48**, 1199 (1926).

[32] Maier and Ralston, *J. Am. Chem. Soc.*, **48**, 364 (1926); Maier, Parks and Anderson, *J. Am. Chem. Soc.*, **48**, 2564 (1926).

[33] Gillespie and Hall, *J. Am. Chem. Soc.*, **48**, 1207 (1926).

[34] Hill and Malisoff, *J. Am. Chem. Soc.*, **48**, 918 (1926).

[35] Cox and Cretcher, *J. Am. Chem. Soc.*, **48**, 451 (1926); Cox, Nelson and Cretcher, *J. Am. Chem. Soc.*, **49**, 1080 (1927).

[36] Hall, Robb and Coleman, *J. Am. Chem. Soc.*, **48**, 927 (1926); Scott and Frazier, *J. Phys. Chem.*, **31**, 459 (1927); Archibald and Hallett, *J. Am. Chem. Soc.*, **47**, 1314 (1925); Sarver and Brinton, *J. Am. Chem. Soc.*, **49**, 943 (1927); Williams, Fogg and James, *J. Am. Chem. Soc.*, **47**, 297 (1925); James, Fogg, McIntire, Evans and Donavan, *J. Am. Chem. Soc.*, **49**, 132 (1927); Crew, Steinert and Hopkins, *J. Phys. Chem.*, **29**, 34 (1925).

[37] Smith, *J. Am. Chem. Soc.*, **47**, 762 (1925).

[38] Fenwick, *J. Am. Chem. Soc.*, **48**, 860 (1926).

[39] Ward, *J. Phys. Chem.*, **30**, 1316 (1926).

[40] Dorfman and Hildebrand, *J. Am. Chem. Soc.*, **49**, 729 (1927).

[41] Collett and Johnston, *J. Phys. Chem.*, **30**, 70 (1926).

zenes.[42] Much more work of this type will be needed to elucidate the matter; and this should, in the writer's view, be done largely with organic compounds, as solutes or as solvents, by reason of the ease with which the character of the components may by substitution and transposition of groups be altered by small steps. Two conclusions, which promise to be generally valid, may be mentioned: that ortho- meta- and para- XY benzene form solutions with one another which are substantially ideal and therefore their mutual solubilities may be predicted; and that solid solution does not occur between pairs of disubstituted benzenes in which the relative position of the two groups is not the same.

Systems of More Than Two Components. From the Fixed Nitrogen Laboratory [43] there are data on the solubility of a mixture of hydrogen and nitrogen, in the ratio of 3:1, at various pressures in liquid ammonia at a series of temperatures; the concentration of ammonia in the gas phase, which was also determined, proved to be more than six times the value calculated from the vapor pressure of the ammonia, thus constituting a direct example of the error which may creep in through neglect of the influence of pressure upon the activity of a phase. From the same laboratory appeared measurements of the partial pressure of carbon dioxide, ammonia and water in equilibrium with aqueous solutions of ammonium nitrate and carbonate. The partial pressure of carbon dioxide over aqueous solutions of the carbonates and chlorides of potassium, sodium and lithium has also been determined over a range of concentrations in connection with an investigation of the carbonate-bicarbonate equilibrium.[44] The vapor pressure of water in equilibrium with a pair of adjacent salt hydrates (including the pair lowest hydrate-anhydrous salt) may be determined [45] by measuring the pressure over a solution saturated with both hydrates, this being made feasible at temperatures below the ordinary transition temperature of the pair by the addition of a third substance; the result is independent of what this third substance is, so long as both solid hydrates are stable in contact with the solution. In connection with this work, observations were made of the lowering of the transition temperature of sodium sulfate decahydrate-anhydrous by sodium halides.

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[42] Johnston, *J. Phys. Chem.*, **29**, 882 (1925); Andrews, Kohman and Johnston, *J. Phys. Chem.*, **29**, 914 (1925); Andrews, *J. Phys. Chem.*, **29**, 1041 (1925); Kohman, *J. Phys. Chem.*, **29**, 1048 (1925); Kohman and Andrews, *J. Phys. Chem.*, **29**, 1317 (1925).

[43] Larson and Black, *Ind. Eng. Chem.*, **17**, 715 (1925); *J. Am. Chem. Soc.*, **47**, 1015 (1925); Clark and Krase, *Ind. Eng. Chem.*, **19**, 205 (1927).

[44] Walker, Bray and Johnston, *J. Am. Chem. Soc.*, **49**, 1235 (1927).

[45] Norton and Johnston, *Am. J. Sci.*, **12**, 467 (1926); **12**, 477 (1926).

The solubility of silver chloride and of lead chloride [46] in various salt solutions at 25° was examined; the system $AgBr$-KBr-H_2O was studied [47] over the temperature range 13-100°. Other ternary systems studied are: RCl-$CoCl_2$-H_2O ($R = Na, K, Rb, Cs$); [48] $NaNO_3$-Na_2SO_4-H_2O; [49] K_2CO_3-$KHCO_3$-H_2O; [50] K_2CO_3-Na_2CO_3-H_2O; [51] CuO-SO_3-H_2O; [52] As_2O_5-BaO-H_2O; [53] $AgClO_4$-pyridine-H_2O; [54] $AgClO_4$-toluene-H_2O; [55] NaI-acetone-H_2O; [56] $RaSO_4$-$BaSO_4$-H_2O; [57] ester-acid-H_2O; [58] $Zn(OH)_2$-NH_4OH-H_2O; $Zn(OH)_2$-$NaOH$-H_2O.[59]

On the directly practical side we have a system of treatment of boiler water based upon the equilibrium in the system calcium carbonate-calcium sulfate-hot water; [60] for, from the solubility data, dosage of soda can be so regulated that the calcium is precipitated as the loose flocculent carbonate instead of in part, or wholly, as sulfate which forms a hard adherent scale. This is therefore another field in which knowledge is beginning to replace empiricism.

Turning to non-aqueous solvents we may mention a paper on a method for the determination of small amounts of water in methyl alcohol based upon observation of turbidity in the system CH_3OH-H_2O-R ($R =$ ligroin, or hexane); [61] another on the solubility of sulfur and of selenium in solutions of lithium, sodium and potassium in liquid ammonia; [62] a third on the reduction of metals from their salts in solution in liquid ammonia; [63] and a fourth on the determination of transition points in pyridine solution based on potential measurements.[64] This field of work is thus not very popular—though perhaps it is as popular as it deserves to be—unless we include in it systems of earth metal oxides and of metals, which are dealt with elsewhere in this volume.

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[46] Kendall and Sloan, *J. Am. Chem. Soc.*, **47**, 2306 (1925).
[47] Lambert, *J. Phys. Chem.*, **30**, 973 (1926).
[48] Foote, *Am. J. Sci.*, **13**, 158 (1927).
[49] Foote, *Am. J. Sci.*, **9**, 441 (1925).
[50] Hill and Hill, *J. Am. Chem. Soc.*, **49**, 967 (1927).
[51] Hill and Miller, *J. Am. Chem. Soc.*, **49**, 669 (1927).
[52] Bell and Murphy, *J. Am. Chem. Soc.*, **48**, 1500 (1926).
[53] Hendricks, *J. Phys. Chem.*, **30**, 248 (1926).
[54] Macy, *J. Am. Chem. Soc.*, **47**, 1031 (1925).
[55] Hill and Miller, *J. Am. Chem. Soc.*, **47**, 2702 (1925).
[56] Macy and Thomas, *J. Am. Chem. Soc.*, **48**, 1547 (1926).
[57] Doerner and Hoskins, *J. Am. Chem. Soc.*, **47**, 662 (1925).
[58] Kendall and King, *J. Chem. Soc.*, **127**, 1778 (1925).
[59] Dietrich and Johnston, *J. Am. Chem. Soc.*, **49**, 1419 (1927).
[60] Hall, *Ind. Eng. Chem.*, **17**, 283 (1925); Hall, Otto and Jackson, *Ind. Eng. Chem.*, **17**, 409 (1925).
[61] Rising and Hicks, *J. Am. Chem. Soc.*, **48**, 1929 (1926).
[62] Bergstrom, *J. Am. Chem. Soc.*, **48**, 146 (1926).
[63] Kraus and Kurtz, *J. Am. Chem. Soc.*, **47**, 43 (1925).
[64] Mason and Mathews, *J. Phys. Chem.*, **29**, 1507 (1925).

It is difficult to discover any special tendency in recent American work on phase equilibria, or to suggest any particular direction in which research would be most profitable. I might however venture the statements that in many cases an extension of the investigation to cover a wider range of conditions would be advantageous; that, on this basis, much remains to be done with even the most common substances; and that sufficient attention is not always paid to the purity of the substances and to the definiteness and reproducibility of the phases concerned.

Chapter IV.

Thermodynamics of Chemical Reactions.

(Free energy, Entropy)

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A very large proportion of the papers dealing with physical chemistry contains data of thermodynamic interest. For instance measurements of equilibrium, vapor pressure, freezing point, osmotic pressure, solubility, conductivity of solutions, electromotive force, pressure, volume and phase relations are all of importance to thermodynamics. Since many of these subjects are more properly treated in separate chapters this review will be restricted to papers which deal explicitly with free energy and entropy, merely listing some of the more important papers dealing with subsidiary subjects.

It is becoming increasingly evident that entropy and heat of formation are the two most fundamental and useful thermodynamic properties of substances. Entropy is no longer "a quantity to be eliminated from thermodynamic equations as rapidly as possible" but is recognized to be a definite physical property which can be readily measured, which follows simple empirical laws, and which can be calculated in simple cases by rigorous theoretical methods.

Great interest still holds in the refinement of these theoretical calculations and their agreement with experiment. The most important American paper in this field is that of Pauling and Tolman [1] who derive theoretical equations for the difference of entropy between a crystal and its supercooled liquid. Their most striking result is that the entropy of a crystal does not depend on the complexity of the molecule or on the crystal form. This contradicts the hypothesis of Eastman and requires that we modify the simple definition of entropy as the logarithm of the number necessary to specify the position and state of motion of each particle in the body. Even in the case of liquids this definition is inadequate for according to Pauling and Tolman a monatomic liquid would have zero entropy at absolute zero. The amount of deviation of the entropy of a liquid from zero at the absolute zero depends on the complexity of the molecule of the liquid. This result makes it of increasing importance to study the entropy of substances at very low temperatures. Unfortunately apparently there are but three places in America where liquid hydrogen is available and only one where liquid helium is available. The University of California appears to be the only place in America where measurements of specific heat have been extended to below liquid air temperatures.[2, 3]

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[1] Pauling and Tolman, *J. Am. Chem. Soc.*, **47, 2148 (1925).**

A group of papers has appeared dealing with the experimental determination of the entropy of gases. Rodebush and coworkers [4] have measured by Knudsen's method the vapor pressure and hence the entropy of the monatomic vapors of sodium and potassium. The agreement with theory is fair. The same method has also been used to measure the vapor pressure and entropy of several alkali halides. Maier [5] has summarized the results of the vapor pressure of zinc and cadmium, finding values for the entropy in almost exact agreement with those calculated from the Sackur-Lewis equation.

A new method of measuring the degree of dissociation of diatomic vapors was described by Weide and Bichowsky [6] and successfully applied to iodine and bromine vapors by DeVries and Rodebush.[7] The degree of dissociation of diatomic vapors is of particular importance since accurate values of the heat of dissociation of these molecules are obtainable from the vibration limit of the spectrum and since several methods are now available for calculating the specific heat and entropy of these diatomic gases from spectral data. These checks from spectral data are particularly needed as the results of DeVries and Rodebush do not

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[2] Latimer, Buffington and Hoenshel, *J. Am. Chem. Soc.*, **47**, 1571 (1925).

[3] Latimer and Hoenshel, *J. Am. Chem. Soc.*, **48**, 19 (1926).

[4] Rodebush and DeVries, *J. Am. Chem. Soc.*, **47**, 2488 (1926); Fiock and Rodebush, *J. Am. Chem. Soc.*, **48**, 2522 (1926).

[5] Maier, *J. Am. Chem. Soc.*, **48**, 356 (1926).

[6] Weide and Bichowsky, *J. Am. Chem. Soc.*, **48**, 2529 (1926).

[7] DeVries and Rodebush, *J. Am. Chem. Soc.*, **49**, 656 (1927).

check those calculated from the well established equation for the monatomic gases.

The disagreement between the experimental results for the entropy of diatomic gases and the results calculated from the earlier form of the quantum theory has largely disappeared. Hicks and Mitchell[8] have calculated directly from the infra red absorption spectra, the entropy of HCl gas. Their results agree excellently with experiment and this agreement seems definitely to settle the mooted question of the *a priori* weights to be assigned to the quantum states involved.

Birge and Sponer[9] have shown by an analysis of the spectral levels of O_2 and N_2 that the heat of dissociation of these gases are respectively about 7.05 and 11.4 volt equivalents. O_2 therefore should dissociate at tungsten temperatures which agrees with observations of Langmuir.

In the case of those diatomic gases where this method is not available Van Vleck,[10] using the Schrödinger mechanics, has devised theoretically entropy equations for diatomic gases which Hutchisson[11] has shown agrees with the rather unsatisfactory data from the specific heat of H_2.

This is of course just a beginning in the application of the Schrödinger mechanics to chemical problems. The full application of this extremely important theory to chemistry will probably depend on the labor of physicists rather than chemists, due to the regrettable lack of training in modern mathematical methods which still characterizes chemical education nearly everywhere.

The truth of the third law as applied to crystalline solids appears to be generally recognized. The latest determinations which give data checking this law are those of Latimer and Hoenshel[12] on $PbBr_2$ and Br_2 and of Maier and Ralston,[13] and Maier, Parks and Anderson[14] on ZnO. The first authors made determinations of the specific heat of $PbBr_2$ and Br_2 down to liquid hydrogen temperatures, while Maier at the Berkeley Bureau of Mines, cooperating with workers at Stanford, measured the important equilibrium ZnO + CO directly at high temperatures, the E.M.F. of the ZnO electrode, the specific heat of ZnO down to low temperatures and the heat of formation of ZnO. The agreement

[8] Hicks and Mitchell, *J. Am. Chem. Soc.*, 48, 1520 (1926).
[9] Birge and Sponer, *Phys. Rev.*, 28, 259 (1926).
[10] Van Vleck, *Phys. Rev.*, 28, 980 (1926).
[11] Hutchisson, *Phys. Rev.*, 28, 1022 (1926).
[12] Latimer and Hoenshel, *J. Am. Chem. Soc.*, 48, 19 (1926).
[13] Maier and Ralston, *J. Am. Chem. Soc.*, 48, 364 (1926).
[14] Maier, Parks and Anderson, *J. Am. Chem. Soc.*, 48, 2564 (1926).

between these several methods of determining entropy is excellent and the work is likely to become a classical example of the complete thermodynamic study of an industrially important process. Dietrich and Johnston[15] have made a careful study of the stability of ZnO and $Zn(OH)_2$, which confirms and amplifies Maier, Parks and Anderson's conclusions.

Webb[16] has determined the heat of formation of AgI. This with known specific heat and E.M.F. data allows the calculation of the entropy of I by four different routes. The values for the entropy per gram atom at 298° are 13.95, 14.05, 14.24 and 13.95 entropy units. This is a fair example of the agreement which is now being obtained.

Less satisfactory agreement exists between the various ways of determining the entropy of calcite and aragonite. Bäckström[17] has measured the heat of formation of calcite and aragonite. This, with his earlier determination of the solubility of these substances and with data on the specific heat and degree of dissociation, allows two checks on the third law. Apparently the specific heat curve for calcite needs redetermination.

Various miscellaneous determinations of entropy by the specific heat method have been made. Rodebush and Michalek[18] measured the specific heat of iron and nickel down to liquid air temperatures. Iron is interesting because of the large and still unexplained deviation from the Debye equation. According to a suggestion of Latimer this is connected with the high thermoelectric effect. Presumably both anomalies are connected with the existence of free electrons in the metal lattice but a satisfactory theory of the metal state is still lacking. This is carefully discussed by Eastman.[19] Parks and Kelley[20] have determined the heat capacity and entropy of MgO, CaO, Al_2O_3, Fe_2O_3, Fe_3O_4 (two forms) and $CaSiO_3$. These data are of great industrial import since they allow calculation of the various equilibria involved in the manufacture of Ca, Mg, Al and Fe. Of even more significance are a series of determination by Parks and coworkers, and by Andrews on the entropy of organic compounds. Parks and coworkers[21] have determined the entropy of the following substances: methyl alcohol, ethyl alcohol, isopropyl alcohol and tertiary butyl alcohol; formic acid, acetic acid, butyric acid, oxalic acid and palmitic acid; glycol, glycerol, mannitol, erythritol, glucose and acetone. This series suggests the rule that the entropies and corresponding free energies are additive and gives us a measure of the specific entropy of the CH_3, CH_2, CHOH, COOH, CO and other groups. We thus have for the first time a method of distinguishing the thermodynamic tendency to react (free energy) of organic substances from their reactivity (rate of reaction). Thus we know that any difference in the rate of oxidation of methyl and ethyl alcohol does not depend on the free energy difference but on differences in the reactivity, while in the case of a secondary and primary alcohol, difference in behavior on oxidation is in part dependent on the difference of the thermodynamic stability of these alcohols. Full extension of these data would remove the question of stability of organic compounds from the realm of personal "hunches" to that of numerical certainty.

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[15] Dietrich and Johnston, *J. Am. Chem. Soc.*, **49**, 1419 (1927).

[16] Webb, *J. Phys. Chem.*, **29**, 816 (1925).

[17] Bäckström, *J. Am. Chem. Soc.*, **47**, 2432, 2443 (1925).

[18] Rodebush and Michalek, *J. Am. Chem. Soc.*, **47**, 2117 (1925).

[19] Eastman, *J. Am. Chem. Soc.*, **48**, 552 (1926).

[20] Parks and Kelley, *J. Phys. Chem.*, **30**, 47, 1175 (1926).

[21] Parks and Anderson, *J. Am. Chem. Soc.*, **48**, 1506 (1926); Parks and Kelley, *J. Am. Chem. Soc.*, **47**, 2089 (1925).

Andrews[22] and Andrews, Lynn and Johnston[23] have made similar studies of the specific heat of disubstituted benzenes. Andrews used a novel method of measurement, but did not extend his measurements below 110°A and because of the unexplained shape of his curves (almost linear) his results cannot be extrapolated with entire safety to give absolute entropies, though relative values are readily found. His general result is that the *o*-, *p*-, and *m*-derivatives have the same entropy except near the melting point. Therefore the difference of behavior of these isomers does not depend on thermodynamic differences.

Another important line of investigation is found in Latimer's[24] and Latimer and Buffington's[25] calculation of the entropy of aqueous ions. This quantity appears to be closely related to the size of the ions and less specifically to hydration than might be suspected, though, of course, size of ions is itself connected with degree of hydration. It is quite likely in the future we shall prefer to express the thermodynamic property of ions in terms of their entropy rather than free energy or electrode potential for the reason that entropy is everywhere proving to be the property most susceptible to theoretical calculation, and most likely to obey simple empirical rules. For example Bruzs[26] has recently shown the entropy of all elements at their melting point is about 20 while there are well known empirical rules which allow the estimate of the entropy of solid and gaseous compounds. No such simple rules hold for free energy. There have been numerous investigations of equilibrium by methods not involving the third law. Maxwell and Hayes[27] studied the equilibrium between Fe and C to give FeC_3. This problem is of such industrial importance that the wonder is that it was not studied years ago. Of industrial importance also are the investigations of Guernsey and Sherman[28] on the decomposition of sodium cyanide and sodium carbide and of Pease and Cook[29] of the reaction $NiO + H_2$. Cantelo[30] has continued his studies on CH_4 and Prescott, Jr.,[31] has made a beginning in the physical chemistry of zirconium in his interesting investigation of the reduction of zircon with carbon to form zirconium carbide. Burrows and Lucarini[31a] have studied the equilibrium between benzene, hydrogen and cyclohexane. Their results are consistent with thermal data and with the Nernst approximation formula. It is unfortunate that the specific heat of cyclohexane at low temperatures is not known. We need all possible checks of the third law for organic reactions involving heavy molecules. Gillespie and Hall[32] have contributed a study of the system $H_2 + Pd$ proving the existence of the definite compound Pd_2H, and giving its free energy and heat of formation. Boyd, Lovell and Coleman[33] have made the observation that the exhaust gases from a gasoline engine have an equilibrium composition.

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[22] Andrews, *J. Am. Chem. Soc.*, 48, 1287 (1926).
[23] Andrews, Lynn and Johnston, *J. Am. Chem. Soc.*, 48, 1274 (1926).
[24] Latimer, *J. Am. Chem. Soc.*, 48, 1234 (1926).
[25] Latimer and Buffington, *J. Am. Chem. Soc.*, 48, 2297 (1926).

All measurements of electromotive force of cells give or should give a measure of the free energy of some chemical reaction, if only that of a concentration cell. We shall, however, exclude from treatment here those E.M.F. measurements whose primary interest is as a measure of the activity of electrolytes, as these measurements are more properly discussed elsewhere. The E.M.F. determinations of most interest here are those of Miss Fenwick,[34] who calculates the molal electrode potentials of Cu, Cu^+ to be

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[26] Bruzs, *J. Phys. Chem.*, **31**, 681 (1927).
[27] Maxwell and Hayes, *J. Am. Chem. Soc.*, **48**, 584 (1926).
[28] Guernsey and Sherman, *J. Am. Chem. Soc.*, **48**, 140, 695 (1926).
[29] Pease and Cook, *J. Am. Chem. Soc.*, **48**, 1199 (1926).
[30] Cantelo, *J. Phys. Chem.*, **30**, 1641 (1926); **31**, 124, 246, 417 (1927).
[31] Prescott, Jr., *J. Am. Chem. Soc.*, **48**, 2534 (1926).
[31a] Burrows and Lucarini, *J. Am. Chem. Soc.*, **49**, 1157 (1927).
[32] Gillespie and Hall, *J. Am. Chem. Soc.*, **48**, 1207 (1926).
[33] Boyd, *Ind. Eng. Chem.*, **17**, 1216 (1925); Lovell, Coleman and Boyd, *Ibid.*, **19**, 373, 376 (1927).
[34] Fenwick, *J. Am. Chem. Soc.*, **48**, 860 (1926).

— 0.522 and of Cu^+, Cu^{++} to be — 0.167 volt. She worked largely with solutions of the perchlorate and made careful study of the activity of the solutions and her values supersede that of earlier workers. Brown and Tefft [35] have studied the MnO_2 electrode, determining the oxidation potential $MnO_2 \rightarrow MnO_4^-$. Morgan and Hildebrand [36] attempted to find the potential of the fluorine electrode by obtaining the limiting value of the polarization voltage of a platinum electrode in KHF mixtures. Their values are not in accord with entropy determination by Latimer,[37] and further work is needed. Hampton [38] has made a careful study of the electromotive force of the iron electrode, which study is of importance not only for itself but because the methods used are of interest to all working with electrodes of "hard" metals.

Various vapor pressure determinations have been made on pure compounds. Harvey and Schuette [39] have studied S_2Cl_2; Noyes and Wobbe,[40] $H_2C_2O_4$; Miss Andrews,[41] naphthalene; Rushton and Daniels,[42] As_4O_6; Berliner and May,[43] nitroanilines; Swan and Mack,[44] various organic compounds; Fiock and Rodebush,[45] K and alkali halides; Perry and Bardwell,[46] C_2N_2; and Perry and Porter,[47] HCN. Mathews [48] has measured the heat of vaporization of some 50 organic compounds. These with the known boiling points are equivalent to vapor pressure determinations.

It is futile to list here researches which might be done in applied thermodynamics. Some of the more important have been indicated in the text. What is needed most of all is the extension of the new spectral and quantum theory methods of calculating entropies and the systematic extension of data on entropy, free energy and especially on heats of reaction.[49] As has been pointed out organic chemistry is almost a virgin field for the thermodynamicist. The thermodynamics of the compounds of P, Cr, V, Mn, Fe, Co, Ni, Sb, Sn, Pb, Si, Al and Ca is almost unknown. The thermodynamics of the metallurgy of Cu, Zn and Pb is still uncertain. Even the chamber process for sulfuric acid is hardly understood though in these days of competition with the contact process it would surely pay some chamber people to investigate it.

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[35] Brown and Tefft, *J. Am. Chem. Soc.*, **48**, 1128 (1926).
[36] Morgan and Hildebrand, *J. Am. Chem. Soc.*, **48**, 911 (1926).
[37] Latimer, *J. Am. Chem. Soc.*, **48**, 2868 (1926).
[38] Hampton, *J. Phys. Chem.*, **30**, 980 (1926).
[39] Harvey and Schuette, *J. Am. Chem. Soc.*, **48**, 2065 (1926).
[40] Noyes and Wobbe, *J. Am. Chem. Soc.*, **48**, 1882 (1926).
[41] Andrews, *J. Phys. Chem.*, **30**, 1497 (1926).
[42] Rushton and Daniels, *J. Am. Chem. Soc.*, **48**, 384 (1926).
[43] Berliner and May, *J. Am. Chem. Soc.*, **47**, 2350 (1925).
[44] Swan and Mack, *J. Am. Chem. Soc.*, **47**, 2112 (1925).
[45] Fiock and Rodebush, *J. Am. Chem. Soc.*, **48**, 2522 (1926).
[46] Perry and Bardwell, *J. Am. Chem. Soc.*, **47**, 2629 (1925).
[47] Perry and Porter, *J. Am. Chem. Soc.*, **48**, 299 (1926).
[48] Mathews, *J. Am. Chem. Soc.*, **48**, 562 (1926).
[49] Bichowsky, *Ind. Eng. Chem.*, **18**, 417 (1926).

Chapter V.

Colloid Chemistry.

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The following résumé deals primarily with the contributions of American chemists to the general theory of colloid chemistry. Since the last survey was written the proceedings of the Fourth National Colloid Symposium held in Cambridge, Mass., June 23-25 (1926) have been published.[1] Special attention is called to these annual volumes which give a detailed account of a number of the important investigations of American workers in this field.

Colloidal Solutions. *Stability.* McBain in "A Survey of the Main Principles of Colloid Science"[2] gives a comprehensive discussion of the factors influencing the stability of sols under the following headings: Gibbs theorem, conception of oriented and polar groups, solvation, the Helmholtz double layer, the resemblance between sols and electrolytes, the Donnan distribution law, the Hofmeister series. The similarities between sols and electrolytes are stressed as is the importance of the Hofmeister series effects. The universal validity of the Donnan distribution law is pointed out but at the same time, attention is called to the grossly exaggerated claims of Loeb and others as to the part the Donnan equilibrium plays in colloidal behavior. Randall, McBain and White[3] have calculated the activity coefficients of soap solutions. These data furnish further evidence to support the theory that the soaps are colloidal electrolytes which yield micelles in more concentrated solutions.

Since recent work of Milner,[4] Debye[5] and others indicates the existence of a mutual action of ions in solutions, Burton[6] is led to assume a similar mutual action of charged particles and an interaction of such colloidal particles and ions in solution. Most writers neglect this mutual action of charged particles and cling to the old idea of the Helmholtz double layer, *viz.*, that immediately surrounding a charged wall or particles in contact with a liquid, there is a layer of oppositely charged ions, the thickness of the layer being of *molecular* dimensions. As a result of the work of Milner, who calculated the thickness of the outer Helmholtz double layer and its relation to the molality of the solution and the valence of the ions in solutions, Burton gives a picture of the charged colloidal particle with its surface charge and surrounding atmosphere of liquid containing positive and negative ions, and explains the stability of sols, the Schulze-Hardy law, and the motion of particles in an electric field.

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[1] Colloid Symposium Monograph, Vol. 4. New York, Chemical Catalog Co., 1926.
[2] Colloid Symposium Monograph, 4, 7 (1926).
[3] *J. Am. Chem. Soc.*, **48**, 2517 (1926).
[4] *Phil. Mag.*, 23, 551 (1912); 25, 742 (1913); *Trans. Faraday Soc.*, **15**, 148 (1919).
[5] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

From ultramicroscopic examination of arsenious sulfide sol Weiser[7] showed that small amounts of alkali chlorides desensitize the sol, causing partial agglomeration. The greater precipitation value of barium chloride for arsenious sulfide sol in the presence of alkali chloride is not due primarily to the stabilizing action of the chloride ion[8] but to the effect of each cation on the adsorption of the other (cationic antagonism). From a survey of ionic antagonism in inorganic and biological systems, Weiser[9] suggests that the antagonistic action of salt pairs on protoplasm is determined by their effect on the permeability of the cell membrane. The membrane of a living cell may be a colloidal film similar to a colloidal sol that can undergo reversible coagulation. If so, there would appear to be a close analogy between the action of salt pairs toward such sols as copper ferrocyanide and arsenious sulfide and the antagonistic action of salt pairs on the permeability and hence on the life and growth of living cells. Observations of McClendon[10] support the contention of the existence of a colloidal semipermeable membrane on the cell surface. In this connection Rice[11] has continued his investigation on equilibrium in colloid systems. Assuming that the surface tension[12] and other properties of colloidal particles do not vary with their size, Rice shows that dispersion is a stable state if the surface tension is large and coagulation is a stable state if the surface tension is small. Dispersed systems will coagulate at certain definite concentrations and potentials of the particles such that the surface tension is zero. Rice[13] shows further that, where a surface is extended, the dynamic surface tension is greater than the static and when the surface is contracted, is less. It is suggested that equilibrium might be established between all parts of the solvent but not between the portions of the solute which are respectively near and far from it. It is shown that the narrower the region to which adsorption is confined after equilibrium is established, the larger will be the value of the dynamic surface tension. If perfect solution laws hold clear to the surface, the dynamic surface tension can never be greater than the surface tension of the pure solvent unless the adsorption is positive; but if the adsorption is negative, an infinite value of the dynamic surface tension is theoretically possible. It is claimed that du Noüy's method[14] of the ring tensimeter does not give true static values of the surface tension.

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[6] Colloid Symposium Monograph, 4, 132 (1926).
[7] *J. Phys. Chem.*, 30, 1527 (1926).
[8] *Cf.* Ghosh and Dhar, *J. Phys. Chem.*, 31, 649 (1927).
[9] Colloid Symposium Monograph, 4, 354 (1926).
[10] Colloid Symposium Monograph, 4, 224 (1926).
[11] *J. Phys. Chem.*, 30, 1660 (1926).
[12] Rice, *J. Phys. Chem.*, 30, 1348 (1926).

In agreement with Lottermoser,[15] Sheppard and Lambert[16] showed that neutralization by adsorption or electro adsorption is a phase of silver halide precipitations. The process is not purely one of recrystallization as suggested by Jablczynski.[17] The coagulation is inhibited by gelatin. The higher the concentration of the gelatin, the higher the total concentration of reactants at which flocculation is possible. Flocculation plays only a subordinate role in the grain growth of silver halide emulsions.[18]

Since the solution pressure of $BaSO_4$ at 100° ceases to be a function of particle size for particles larger than about 2 microns in diameter, Trimble[19] concludes that the coalescence of barium sulfate precipitates on digestion is due to collection of the particles into aggregates, which subsequently become cemented together.

Yoe and Freyer[20] studied the effect of hydrogen ion concentration on the viscosity of hydrous oxide sols. With increasing pH, there is little change in viscosity until around $pH = 7$, when there is a marked increase to a maximum, followed by a sharp decrease to a nearly constant value. The change in viscosity is attributed to variation in the decrease of "hydration" in its most general sense.

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[13] *J. Phys. Chem.*, **31**, 207 (1927).

[14] *Phil. Mag.*, **48**, 264 (1924).

[15] *J. prakt. Chem.*, 72, 39 (1905): *Kolloid-Z.* (Zsigmondy Festschrift), **36**, 230 (1925); *Z. angew. Chem.*, **39**, 347 (1926).

[16] Colloid Symposium Monograph, **4**, 281 (1926).

[17] *Bull. soc. chim.*, **33**, 1592 (1923).

[18] Attention should be called to Sheppard's interesting papers on the chemistry of photography, *J. Chem. Education*, **4**, 298, 465 (1927).

[19] *J. Phys. Chem.*, **31**, 601 (1927).

[20] *J. Phys. Chem.*, **30**, 1389 (1926).

Preparation. Sulfur sols in benzene, toluene, kerosene, xylene, acetone and ethyl acetate were prepared by Garard and Colt [21] by the interaction of hydrogen sulfide and sulfur dioxide. The benzene sol was quite stable even in the presence of electrolytes and the organic substances which were tried as coagulants. Byron [22] observed that pyroxylin is not peptized by anhydrous ether at any temperature but it is peptized by alcohol at low temperatures. The peptization is due to adsorption of polymerized alcohol. The peptizing action of alcohol-ether mixtures is greater than that of pure alcohol owing to polymerization of alcohol by the ether.

Telkes [23] describes an apparatus for the electrical dispersion of lead in the absence of oxygen and carbon dioxide which render the sol instable. The purpose of the research was to prepare a stable lead sol which might be used for intravenous injection in the treatment of cancer.[24]

Gels. Benton [25] prepared a jelly of metallic platinum by allowing a fairly concentrated sol of platinum to stand quietly. The jelly possessed elastic properties and exhibited syneresis. This is of particular interest for the theory of jelly formation and indicates that any substances which will adsorb another liquid strongly can be obtained as a jelly under suitable conditions.[26]

Williams and Skogstrom [27] describe the formation of gels of phosphorus pentoxide in nitromethane with water, organic acids, aldehydes, ketones and alcohols and peptizing agent. There is a definite concentration of peptizing agent above and below which a gel will not form. Apparently the pentoxide in a finely divided condition reacts chemically with the peptizing agent giving a protecting film around each particle. These agglomerates are then held in a regular gel structure. In an extended paper on the organophile colloids, Whitby [28] discusses the conditions of formation of gels of substances by swelling in organic liquids. Among the substances investigated are rubber and the cellulose esters, metastyrene, higher cellulose esters and cellulose ethers, phytosterolin and silver soaps.

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[21] *J. Am. Chem. Soc.*, 49, 630 (1927).
[22] *J. Phys. Chem.*, 30, 1116 (1926).
[23] *J. Am. Chem. Soc.*, 49, 1382 (1927).
[24] Bell and others, *Lancet*, 1, 537 (1926).
[25] *J. Phys. Chem.*, 30, 1415 (1926).
[26] *Cf.* Weiser, "The Hydrous Oxides," p. 15. New York, McGraw-Hill, 1926.
[27] *J. Phys. Chem*, 30, 1170 (1926).
[28] Colloid Symposium Monograph, 4, 203 (1926).

Spencer [29] studied the conditions of forming pectin jellies and showed the usual statement to be inaccurate, that syrups are not formed in acid jellies when the sugar concentration is too high or the acid concentration is too high. Failure of people to form jellies under the above conditions is due to hydrolysis. The acid jelly field is in reality a continuous one above the syrup-jelly boundary and syrup only exists below the boundary. The theory of pectin gelation is as follows: Pectin is peptized by water, acid displaces water to some extent and sugar replaces both water and acid to some extent. The boundary of the jelly region is accounted for by the partial displacement of water by acid followed by the further displacement of water by sugar. Thus where acid is low more sugar is required to form a jelly than where acid is high.[30]

Browne and Truax [31] define a "glue" as any material which can be obtained as an emulsoid sol of suitable consistency, which wets a particular surface and which subsequently forms a strong elastic jelly by cooling, heating, evaporation or chemical reaction. Both mechanical adhesion and specific adhesion are operative in the gluing of wood. Specific adhesion does not presuppose positive adsorption of the glue from the sol by wood.

Investigations on rhythmic banding in gels have been carried out by Davies and Sivertz [32] and by Riegel and Reinhard.[33] The former prepared rhythmic diurnal bands of gold and platinum in silica gel and showed that the diurnal bands result from the light reduction of alternate zones followed by diffusion. The latter investigators studied the zone pattern of silver dichromate in gelatin. In washed gelatin the dichromate forms no line but an unbroken deposit exhibiting a zone pattern which is free from lines. Addition of a small amount of sodium chloride to a solution of the washed gelatin causes a reappearance of red bands. Hence red bands form only in the presence of the substructure provided by the chloride impurity.

In this connection attention may be called to Eckert and France's observation [34] that the presence of gelatin in solutions of copper sulfate and lead nitrate produces a marked decrease in the average size of crystals formed during evaporation. Increasing concentrations of gelatin increase the uniformity of the size of crystals. There appears to be a similarity in the action of gelatin as affecting microscopic crystals formed either by electro or chemical precipitation, on the one hand, and macroscopic crystals grown from aqueous solution by evaporation, on the other.

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[29] Colloid Symposium Monograph, **4**, 203 (1926).

[30] *Cf.* also Ohn, *Ind. Eng. Chem.*, **18**, 1295 (1926).

[31] Colloid Symposium Monograph, **4**, 258 (1926); *cf.* Weinstein, *ibid.*, **4**, 270 (1926).

[32] *J. Phys. Chem.*, **30**, 1467 (1926).

[33] *J. Phys. Chem.*, **31**, 713 (1927).

[34] *J. Phys. Chem.*, **31**, 877 (1927).

Emulsions. Stamm and Kraemer[35] suggest that the formation of an emulsion by shaking, mixing, etc., may be considered as consisting of two stages: a pulverization of both phases into lamellae and drops and a coagulation or reunion of the drops of one or both phases. The function of an emulsifying agent is more or less to prevent the drops of one phase already formed in the pulverizing stage from coagulating, while allowing the other drops to coagulate giving the dispersion medium. Davey[36] pictures an ordinary emulsion of the water-in-oil type as having a gel-like structure in which "bristles" of the emulsifying agent such as soap from one oil droplet tend to interlock with "bristles" from an adjacent oil droplet to give the characteristic stiff structure of the oil phase of such an emulsion. The water is held in the interstices between the chains of oil drops by the remaining free "bristles." By the aid of this picture, several methods are outlined for the making and breaking of emulsions. Mead and McCoy[37] investigated the effect on the oil-water interfacial tension of solutions of oil-soluble emulsifying agents which form water-in-oil emulsions such as the oil technologist is confronted with. The emulsifying agents investigated were oleic and stearic acids and zirconium and aluminum stearates.

Adsorption. Miller[38] gives a detailed account of methods for the preparation of a standard adsorbent charcoal which has but a few hundredths of one % or less of ash. All the adsorbent charcoals after purification have the same properties of selective adsorption from solutions of electrolytes. The adsorbent properties are identical with those of pure ash-free activated sugar charcoal. All pure adsorbent charcoals adsorb salts hydrolytically, the acid being adsorbed but not the inorganic hydroxides. In this connection Thomas and LeCompte[39] report that purified charcoals have no

[35] *J. Phys. Chem.*, 30, 992 (1926).
[36] Colloid Symposium Monograph, 4, 38 (1926).
[37] Colloid Symposium Monograph, 4, 44 (1926).
[38] *J. Phys. Chem.*, 30, 1031, 1162 (1926).
[39] Colloid Symposium Monograph, 4, 328 (1926).

adsorbing action on ferric oxide sols. The removal power of technical charcoals on ferric oxide sols is not due to adsorption but to the precipitating action of the electrolyte impurities. Pure charcoals have almost a negligible adsorbing power on ferric chloride solution at least in concentrations up to 0.02 molar. Coolidge[40] found the adsorption of water by pure charcoal to be quite small, and to be greatly increased by traces of inorganic impurities. In pure charcoal, Henry's law holds below a relative pressure of one-tenth; above this, the pressure increases less than proportionately to the concentration. The adsorption of water vapor reaches a maximum at the triple point. The heat of adsorption at ordinary temperatures is nearly constant and nearly equal to the latent heat of evaporation of liquid water. It increases slightly as the concentration increases. The partial molal heat capacity of adsorbed water at low concentrates is 38 calories per mol. The characteristic adsorption isotherms of non-polar substances such as benzene, ether and chloroform are concave toward the axis of pressures while those of polar substances such as water and ammonia are partially convex toward the axis of pressures. Lowry and Kohman[41] showed that the most important factor determining the amount of water absorbed by a given sample of rubber is the vapor pressure of water with which it is in equilibrium. It is believed that the absorption consists of two processes: the formation of a true solution of water in rubber and the formation of solutions internal to the rubber of the water soluble constituents of the rubber.

Coolidge[42] examined the condensation theory of adsorption[43] by porous adsorbents and found it quite inadequate to account for observed facts without the aid of *ad hoc* assumptions. The relation between heats of adsorption and slopes of the isosteres is discussed. The Clausius-Clapyron equation has been found to hold within a few %. The heat of adsorption appears to be due to the work done by the attractions of the adsorbent plus the ordinary latent heat of condensation. Dew and Taylor[44] determined the adsorption and heat of adsorption of ammonia gas on metallic catalysts. An apparent relationship between heat of adsorption and catalytic activity is presented in the case of the reaction $2NH_3 = N_2 + 3H_2$.

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[40] *J. Am. Chem. Soc.*, **49**, 708 (1927).
[41] *J. Phys. Chem.*, **31**, 23 (1927).
[42] *J. Am. Chem. Soc.*, **48**, 1795 (1926).
[43] McGavack and Patrick, *J. Am. Chem. Soc.*, **42**, 946 (1920).
[44] *J. Phys. Chem.*, **31**, 277 (1927); *cf. also* Beebe, *ibid.*, **30**, 1538 (1926).

This will be discussed further in the section of this survey dealing with catalysis.[45]

Frazer, Patrick and Smith[46] showed that the thickness of the adsorbed film of toluene on a plane surface is never greater than unimolecular even at saturation pressures. If this is generally true, the theories of adsorption proposed by Eucken and Polyani are rendered untenable since the essence of their theories is that the adsorbed layer is multimolecular in thickness. Evidence is presented to show that water vapor reacts with fresh glass surfaces so that washed glass does not present a plane surface. Continuing his observations on the adsorption of vapors by gels, Perry[47] finds that the gel of hydrous ferric oxide adsorbs most vapors as effectively as the gels of alumina and silica.

In discussing the mechanism of adsorption and swelling of elastic gels, Terzaghi[48] points out that the discrepancy between the measured swelling pressure and the calculated values from the vapor pressure formula, can be accounted for by the fact that the lowering of vapor pressure in the pores of the adsorbent is due not to a single cause but to two essentially different causes: A tension P_1 in the liquid and a change P_2 in the molecular energy of the liquid. The first gives the measured swelling pressure which is due to the elastic expansion of the solid phase, previously held under compression by the surface tension of the water; and the second is the result of a change in the internal energy of the liquid which enters the gel. This change is apparently due to the free vibration of molecules of the liquid being reduced to forced ones with a considerably smaller intensity.

From the heat of wetting of silica, Nutting[49] calculated the maximum pull exerted by silica on water is approximately 17,000 atmospheres, which is of the order of the tensile strength of quartz. By means of X-ray analysis Posnjak[50] showed conclusively that the so-called alpha and beta stannic acids are identical and are essentially stannic oxide with adsorbed water. The difference is in the size of the particles, the alpha oxide consisting of smaller particles than the beta. This is but one example of the use of X-rays in the study of colloids. Clark[51] gives a comprehensive survey of the application of X-rays to the study of colloids, especially the technical colloids. In this connection attention should be called to the illuminating contribution of Sponsler and Dore [52] on "The Structure of Ramie Cellulose Derived from X-ray Studies."

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[45] *See also* Taylor, Colloid Symposium Monograph, 4, 19 (1926).
[46] *J. Phys. Chem.*, 31, 897 (1927).
[47] *Ind. Eng. Chem.*, 19, 746 (1927).
[48] Colloid Symposium Monograph, 4, 58 (1926).
[49] *J. Phys. Chem.*, 31, 531 (1927).
[50] *J. Phys. Chem.*, 30, 1073 (1926).
[51] Colloid Symposium Monograph, 4, 145 (1926).

Reyerson and Swearingen [53] determined the adsorption of hydrogen, carbon dioxide, oxygen, methane and ethane upon silica gel metallized with silver, copper, platinum and palladium.[54]

From observations on the adsorption of mercury ions by metallic mercury, Rosenberg and Stegeman [55] reach the following conclusions with regard to the potential of a flowing mercury electrode: The potential varies (1) with the velocity of flow, the greater the velocity the more negative is the flowing mercury to the stationary mercury; (2) with the length of the stream in contact with the solution containing mercury ions, the shorter the length of the stream the more negative is the flowing mercury. The potential of the flowing electrode against a stationary electrode in $0.1N$ KCl or HCl solution saturated with calomel, approaches 0.53 volt as a minimum. The time required for maximum adsorption of mercury ions at a mercury surface is appreciable. This accounts for the behavior of the flowing electrode.

The setting of plaster of Paris was found by Neville [56] to occur in two stages: (a) adsorption accompanied by a contraction in volume and a slight heat effect whereby the two reactants are brought into chemical contact and (b) a resulting exothermic chemical reaction between the adsorbed liquid and the adsorbent with an increase in volume. The influence of different ions on rate of setting of plaster of Paris is due to their effect on the rate of adsorption of water and their catalytic effect on the subsequent chemical change. The setting of litharge-glycerin cement is likewise a two stage process.[57] The rate of the setting depends on the form of the PbO and the dryness of the glycerin. Water, hydroxyl ions and stirring accelerate setting, while hydrogen ions prevent it.

The taking up of bases by humic acid was found by Kawamura [58] to be comparable to the taking up of bases by stearic acid. It is concluded, therefore, that humic acid should be regarded as a real acid. The chief difference in the behavior of humic and stearic acids is that the humate formed continues to adsorb base while the stearate does not do so appreciably. The NaOH and $Ba(OH)_2$ solutions of humic acid contain a definite chemical compound of the acid.

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[52] Colloid Symposium Monograph, **4**, 174 (1926).
[53] *J. Phys. Chem.*, **31**, 88 (1927).
[54] *Cf. also* Ryerson, Harder, and Swearingen, *J. Phys. Chem.*, **30**, 1623 (1926).
[55] *J. Phys. Chem.*, **30**, 1306 (1926).
[56] *J. Phys. Chem.*, **30**, 1037 (1926).
[57] Neville, *J. Phys. Chem.*, **30**, 1181 (1926).
[58] *J. Phys. Chem.*, **30**, 1364 (1926).

Briggs[59] points out that the ideal deinking agent for removing the carbon ink from news print is some substance, preferably a colloid, which is adsorbed much more strongly by ink than by paper and tends to peptize ink. Soap (sodium oleate) is the best deinking agent yet found, the deinking being complete between concentrations of 0.5 and 5%. If the substance is a colloid and is adsorbed more strongly by paper than by ink, a mordanting action results which tends to bind the ink to the fiber. Such an effect has been observed with albumin.

Fall[60] made a systematic investigation of the detergent action of soaps. The method of evaluating the detergent action suggested by Bancroft consists essentially in forming suspensions of clay or other solids in soap solution followed by determining the amount of sodium chloride which must be added to cause flocculation. Practical application of the method was demonstrated in the evaluation of the detergent action of sodium oleate and some commercial soaps, silicates of soda of different composition, caustic soda and some alkaline salts and mixtures of soap and "addition agents." The relative detergent values of soaps were found to differ with different dirts due to specific adsorption. Maximum surface tension lowering is not a safe criterion for estimation of maximum detergent action.

Proteins. Lewis and Daniel[61] showed that Procter's mass action equation for the reaction of gelatin in acid breaks down completely in the face of Loeb's data obtained at low hydrogen ion concentrations. The discrepancy is attributed to internal interaction of amino groups and carbonyl group in the gelatin itself. A general mass action expression for gelatin and acid systems is derived containing a correction term for internal compensation of the basic and acidic group of gelatin in the neighborhood of the so-called isoelectric point. Rinde[62] showed that Loeb's data on the equilibrium between gelatin solutions and hydrochloric acid fit an equation of the type of Langmuir's adsorption equation. He concludes therefore that the alleged reaction between HCl and gelatin is not a chemical process but an adsorption process. Hitchcock[63] points out, however, that this does not follow necessarily since there is a formal identity between Langmuir's adsorption equation[64] and the law of mass action.

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[59] Colloid Symposium Monograph, 4, 311 (1926).
[60] *J. Phys. Chem.*, 31, 801 (1927).
[61] Colloid Symposium Monograph, 4, 122 (1927).
[62] *Phil. Mag.*, 1, 32 (1926).

From extended observations of the light scattering capacity of aqueous gelatin systems Kraemer[65] showed that the term "gelatin" is applied to materials differing considerably in their behavior even with respect to a property like the isoelectric point, which many people believe to be distinctive. The evidence indicates that any gelatin system consists of an unknown number of unknown components. Hence, theoretical consideration based upon the assumption of the existence of definite and uniform gelatin molecules in aqueous gelatin system would appear rather artificial and formal. Kraemer and Dexter[66] discuss the dispersion of isoelectric gelatin above 30°, (1) as a case of solubility of a phase of constant composition, (*2*) as a case of conjugate solutions with a consolute temperature and (*3*) as colloidal systems with a critical peptization temperature; and arrive at the conclusion that gelatin and other protein systems belong to case (*2*) or (*3*) rather than to case (1). Gortner and Hoffman[67] showed that the rate and extent of inhibition of gelatin particles immersed in water depend on the previous history of the samples. In some instances the initial rate of inhibition appears to be higher in the case of gelatin prepared from sols but the amount inhibited after several hours is greater in gelatin dried down as gels. It is believed that the contrast between the behavior of sol and gel preparations is due in part to the presence of a persistent gel structure. During the process of drying, gelatin sols may develop a more or less fixed structure which is reflected in the subsequent swelling. The existence in the dry state of a sol form which is distinct from a gel form of gelatin was neither proven nor disproven.

Baughman[68] showed that a gelatin sol is completely precipitated by tannin, some tannin remaining in solution in all cases. The highest percentage of tannin present in a 0.5% solution is flocculated by an equal volume of a 0.5% gelatin solution. Beyond this point, the protective action of gelatin on tannin is marked. These observations are of importance in connection with

[63] *J. Am. Chem. Soc.*, **48**, 2870 (1926).
[64] *J. Am. Chem. Soc.*, **40**, 1384 (1918).
[65] Colloid Symposium Monograph, 4, 102 (1926).
[66] *J. Phys. Chem.*, **31**, 764 (1927).
[67] *J. Phys. Chem.*, **31**, 464 (1927).
[68] *J. Phys. Chem.*, **31**, 448 (1927).

the first step in the tanning of leather by tannin. Some further investigations which have to do specifically with the tanning process are reported in the section on leather.[69]

Bancroft[70] points out that the important factor in the peptization of gelatin by potassium iodide may be the displacement of the water equilibrium that exists between hydrol and perhydrol. The same factor may account for the effect of neutral salts on pH values, since there is no satisfactory evidence as yet that the addition of sodium chloride to a dilute hydrochloric acid solution causes any increase in the actual hydrogen ion concentration. It is possible also that the displacement of the water equilibrium is of importance in causing variations from the dilution law. The agreement between potentiometrically determined pH values and those determined by indicators is not an independent confirmation since both depend on the chemical potential of hydrogen ion and not solely on the concentration of hydrogen ion.

Osmosis. A strictly semipermeable membrane separating two liquids consists of a system in which one component is adsorbed with the practical exclusion of the other. The flow of liquid can be from that liquid only which is adsorbed by the membrane. With a carbon membrane consisting of fine pores but not strictly semipermeable, Bartell and Osterhof[71] showed that the initial osmotic force and resulting direction of flow of liquids are determined by the relative adsorption by the membrane material. In such cases the membrane plays an active part and the capillary effect is a deciding factor in determining the initial direction of flow. With a fairly permeable and sufficiently thin membrane, the osmotic flow of a solution in a binary liquid system depends on the properties of the liquid system, rather than on the properties of the membrane.

Stamm[72] studied the electroendosmose through wood membranes. The motion of water was found to be through the microscopic capillaries rather than through the submicroscopic structure. The effective capillary cross section of tangential sections calculated from electroendosmosic measurements corresponds with the values obtained from photomicrographs.

Color. Stillwell[73] showed that the red color imparted to alpha alumina is not due to a higher or lower oxide of chromium or to a change in the concentration of chromic oxide as in the case of chromic salts. The red color is due to alpha alumina and a second modification of chromic oxide of the same crystal structure as the green modification but with an axial ratio nearer to that of alpha alumina than is the axial ratio of the green modification. The occurrence of red or green modifications depends on the axial ratio of the mixed crystal. The bluish-red color of some rubies is due to the reduction of a limited amount of red chromic oxide to blue chromous oxide. The cause of the color of the natural ruby is the same as that of the synthetic product.

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[69] *Cf.* Gustavson, Colloid Symposium Monograph, 4, 79 (1926); *Ind. Eng. Chem.*, 19, 81, 243 (1926); *J. Am. Chem. Soc.*, 48, 2963 (1926); Page and Gilman, *Ind. Eng. Chem.*, 19, 251 (1926).

[70] Colloid Symposium Monograph, 4, 29 (1926).

[71] Colloid Symposium Monograph, 4, 234 (1926).

[72] Colloid Symposium Monograph, 4, 246 (1926).

[73] *J. Phys. Chem.*, 30, 1441 (1926).

Bush[74] finds that silver chromate precipitated from actinized potassium bichromate solutions appears the same as when precipitated from solutions unexposed to light.[75] The color and physical character of the precipitate are determined by the rate of addition of silver salt to the bichromate solution.

Continuing his investigations of the color of insects, Mason[76] finds that the iridescent wing membranes owe their color to multiple thin films separated by material of a slightly different refractive index. Iridescent scales are of three main types, each of which owes its color to multiple thin films separated by air. The fine striations common on insect scales are not related to the iridescence visible under ordinary conditions. Surface color is not exhibited by iridescent insect scales.

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[74] *J. Phys. Chem.*, **31**, 931 (1927).
[75] *Cf. however* Hunt, *Mem. Chem. Soc.*, **2**, 311 (1845).
[76] *J. Phys. Chem.*, **31**, 321 (1927).

Chapter VI.

Catalysis.

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The output of catalytic studies from American centres continues to be large and important, many diverse aspects of the problem being studied. The present report only covers such work as is important from the catalytic standpoint. Numerous papers are published involving catalytic reactions where the subject of catalysis is not important. These are not reported here. They will probably be the object of report in other sections of this Survey. The material collected in this section has been assigned for discussion under several main topics such as theory of the catalytic surface, catalytic oxidation, reduction and the like.

Theory of the Catalyst Surface. Two important studies of this problem involve catalysts for ammonia synthesis. Almquist and Black[1] studied quantitatively the poisoning action of oxygen on iron and various iron-promoted catalysts. Almquist[2] has analyzed these data very effectively to show that only one iron atom in two thousand of a pure iron catalyst possesses any catalytic activity. Even with the best promoted iron catalysts the efficiency only reaches one atom in 200.

Studies of adsorption and of heat of adsorption in reference to catalysis have also resulted in progress. It has been shown by Taylor and Kistiakowsky[3] that copper catalysts show a maximum in the curve for the heat of adsorption of hydrogen on copper when plotted against increasing adsorption. This confirms for copper the result found for nickel by Fryling and is taken to indicate that the most strongly adsorbed hydrogen undergoes also an endothermic activation process, probably a dissociation into atoms.

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[1] *J. Am. Chem. Soc.*, 48, 2814 (1926).
[2] *J. Am. Chem. Soc.*, 48, 2820 (1926).
[3] *Z. physik. Chem.*, 125, 341 (1927); *Proc. Nat. Acad. Sci.*, 13, 1 (1927).

Studies of carbon monoxide adsorption also indicated the possibility of several types of activation surface. Beebe,[4] studying the same subject, suggests, on the basis of some data with mercury-poisoned copper, that the most active spots catalytically may not necessarily be the regions of strongest adsorption activity, but alternatively the areas of medium adsorption where a balance is struck between activation by adsorption and evaporation of the reaction products. Dew and Taylor [5] studied the adsorption and heats of adsorption of ammonia on iron, nickel and copper catalysts and suggested that as the order of decreasing catalytic activity is the order of decreasing heat of low pressure adsorption, the efficiency of catalytic decomposition may be associated with the time interval that an ammonia molecule remains in contact with the metal at a given temperature. The higher the heat of adsorption the longer this time-interval or alternatively the higher the temperature at which the molecule can remain for a given length of time in association with the catalyst atom.

Burk [6] seeks an explanation of the lowering of the heat of activation by a catalyst, in the attachment of both atoms of a reactant AB to the catalyst surface, with the adsorbing atoms arranged spatially to permit this. Taylor [7] associates the newer data on heats of adsorption with simple catalysed decompositions such as those of hydriodic acid and ammonia on platinum, showing that the energy quantities involved in the stepwise catalytic reaction are all much smaller than those involved in the gaseous decomposition. Hoover and Rideal [8] establish the dual nature of oxide catalytic surfaces by showing that the dehydrogenation and dehydration of alcohol on thoria have different energies of activation and that poisoning influences one preferentially. They do not come to any experimental conclusion as to the nature of the two types of surface.

The reduction of so-called irreducible oxides of the type of zinc oxide in presence of a reducible oxide like copper oxide has now been quantitatively demonstrated by Rogers [9] at as low a temperature as 300°C. This observation is of importance in the discussion of the nature of hydrogenation catalysts of the "irreducible oxide type." A study by Pease and Griffin [10] of attempts to activate metallic copper by oxidation and reduction indicates very effectively how exothermic catalytic reaction may destroy a catalyst surface on which only a few labile centres of activity are present.

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[4] *J. Phys. Chem.*, **30**, 1538 (1926).
[5] *J. Phys. Chem.*, **31**, 277 (1927).
[6] *J. Phys. Chem.*, **30**, 1134 (1926).
[7] *Proc. Roy. Soc.*, **113A**, 77 (1926).
[8] *J. Am. Chem. Soc.*, **49**, 104, 116 (1927).
[9] *J. Am. Chem. Soc.*, **49**, 1432 (1927).
[10] *J. Am. Chem. Soc.*, **49**, 25 (1927).

Moisture as Catalyst. The catalysis by glass surfaces of the reaction between nitric oxide and oxygen has been shown by Hasche [11] to depend on the presence of water adsorbed on such surfaces. The use of paraffin surfaces decreased the amount of water surface and also of the catalytic reaction. Sulfur dioxide and nitrogen dioxide were without effect. Lewis and Rideal [12] thought they had shown that intensive drying makes impossible the combination of the halogens with hydrogen, but had no influence on the decomposition of the hydrogen halides. Bodenstein and Jost [13] have shown conclusively that this conclusion rests upon experimental error, the drying agent (P_2O_5) interacting with the hydrogen halide. Also, as Bodenstein and Jost point out, if the results of Lewis and Rideal had been correct a perpetual motion machine would be possible.

Catalytic Oxidation. Probably the most noticeable study of catalytic oxidation during the present year is the work of Benton and Williams [14] on the combination of carbon monoxide and oxygen on quartz glass. Benton and Williams find quartz, when pure, to have a very much smaller catalytic activity than was found by Bodenstein and Ohlmer. Further, they find an entirely different reaction kinetics. This research can therefore be especially commended to the textbook writer and the student of reaction kinetics since this catalysed reaction has hitherto been a favorite example for both. Benton and Williams show that the assumption that a quartz surface is covered with carbon monoxide is experimentally unfounded.

Bray and Doss [15] show that even mixtures of the dried oxides of copper and manganese when ground together subsequently show promoter action in the oxidation of carbon monoxide. Almquist and Crittenden [16] show that reduced copper at 310°C. is preferable even to platinum gauze in the removal of traces of oxygen from hydrogen. Benton and Elgin [17] have studied the catalysis of hydrogen-oxygen mixtures on silver and conclude that the reaction is proportional to the hydrogen pressure independent of the oxygen pressure, inhibited strongly by water vapor. This suggests interaction between hydrogen molecules and oxygen atoms adsorbed on the portions of the silver surface free from adsorbed water. Yant and Hawk[18] have shown that cobaltic oxide is better than either manganese dioxide or nickelic oxide in the catalytic oxidation of methane. Scott and Leach[19] show that cobaltic oxide in association with alumina, bismuth and other oxides shows good conversions in the oxidation of ammonia.

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[11] *J. Am. Chem. Soc.*, 48, 2253 (1926).
[12] *J. Am. Chem. Soc.*, 48, 2553 (1926).
[13] *J. Am. Chem. Soc.*, 49, 1416 (1927).
[14] *J. Phys. Chem.*, 30, 1487 (1926).
[15] *J. Am. Chem. Soc.*, 48, 2060 (1926).
[16] *Ind. Eng. Chem.*, 18, 866 (1926).
[17] *J. Am. Chem. Soc.*, 48, 3027 (1926).

Walton and Christensen[20] have shown that either ferrous or ferric salts are equally good in the oxidation of ethanol to acetic acid by hydrogen peroxide. Ferric acid is an intermediate. Acids retard the reaction rate.

Catalytic Hydrogenation. Hoover, Dorcas, Langley and Mickelson[21] have shown that with a mixed metal catalyst such as Ni-Pd, a 1-3% yield of ethylene from carbon monoxide and hydrogen can be attained at 100°C. and atmospheric pressure. The use of lead as catalyst in the reduction of nitrobenzene by hydrogen has been studied in detail by Madenwald, Henke and Brown.[22] They show that, initially, marked amounts of azobenzene are produced. Adams, Cohen and Rees[23] have studied the catalytic reduction of aromatic nitro compounds with the Adams platinum catalyst. Hiers and Adams[24] have studied the reduction of di- and triphenylamines. Burrows and Lucarini[25] have decisively established the equilibrium between benzene, hydrogen and cyclohexane using platinum as the catalyst. With the latter, side reactions are avoided, in marked contrast to nickel as catalyst.

Catalytic Decomposition. The paper of Hoover and Rideal on alcohol decomposition has already been cited. Small amounts of chloroform were found to promote the ethylene reaction. Pearce and Ott[26] have studied the decomposition of esters in presence of nickel. The reactions are many and complex. That the electrode material decomposes ozone produced in the silent electric discharge has been shown by Newsome.[27] The decomposition occurs at the positive electrode. Decomposition was very marked with aluminium electrodes. Robertson,[28] continuing his studies of promoter action in homogeneous systems, shows that cobalt salts as promoters in the decomposition of hydrogen peroxide in presence of potassium dichromate change the path of the reaction.

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[18] *J. Am. Chem. Soc.*, **49**, 1454 (1927).
[19] *Ind. Eng. Chem.*, **19**, 170 (1927).
[20] *J. Am. Chem. Soc.*, **48**, 2083 (1926).
[21] *J. Am. Chem. Soc.*, **49**, 796 (1927).
[22] *J. Phys. Chem.*, **31**, 862 (1927).
[23] *J. Am. Chem. Soc.*, **49**, 1093 (1927).
[24] *J. Am. Chem. Soc.*, **49**, 1099 (1927).
[25] *J. Am. Chem. Soc.*, **49**, 1157 (1927).
[26] *J. Phys. Chem.*, **31**, 102 (1927).
[27] *J. Am. Chem. Soc.*, **48**, 2035 (1926).

Ionic Catalysis. The relation between ion activity and reaction velocity is being steadily investigated. Brönsted and Livingston [29] have investigated the velocity of ionic reactions with electrolytes of high valence type. Åkerlöf [30] has very thoroughly studied the decomposition of diacetonyl alcohol in alkali-salt solutions and has traced the analogy between the catalytic activity and the ion activity of the hydroxyl ion. Bergstein and Kilpatrick [31] have been investigating the catalytic minimum point and have shown that the results are more in accord with the Brönsted theories than with the theory of activity of dry hydrogen ion. Kilpatrick [32] has studied catalysis in buffered solutions obtaining results in accord with Brönsted's theory of secondary salt effect.

Inhibition and Antioxidants. The influence of antioxidants in the problem of rubber deterioration has been treated generally by Weber.[33] The simultaneous effect of driers and of inhibitors in the oxidation of linseed oil has been studied by Rogers and Taylor.[34] Evidence is given that they exercise their effect independently. It is notable also that the inhibitors are less efficient as inhibitors than a good positive catalyst such as cobalt linoleate is as a catalyst. The inhibitor is more effective at lower temperatures. Reiff [35] has reinvestigated the oxidation of benzaldehyde and concludes that the reaction is heterogeneous, probably occurring at the surface of the containing vessel. He finds that the formation of an active surface by the adsorption of a polar water layer on the wall of the reaction vessel is the chief factor in the oxidation. It is difficult to understand, if this be true, why oxidation occurs so readily in paraffin wax vessels. Also, accelerants of the type of manganese benzoate, which are soluble in benzaldehyde certainly do not suggest by their behavior that the oxidation reaction is a wall reaction. Reiff did not discover that the oxidation is one in which many molecules react per absorbed light quantum and that therefore some chain mechanism is involved, as has been pointed out by Bäckström.[36]

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[28] *J. Am. Chem. Soc.*, **48**, 2072 (1926).
[29] *J. Am. Chem. Soc.*, **49**, 435 (1927).
[30] *J. Am. Chem. Soc.*, **48**, 3046 (1926).
[31] *J. Phys. Chem.*, **30**, 1616 (1926); **31**, 178 (1927).
[32] *J. Am. Chem. Soc.*, **48**, 2091 (1926).
[33] *Ind. Eng. Chem.*, **18**, 963 (1926).
[34] *J. Phys. Chem.*, **30**, 1334 (1926).
[35] *J. Am. Chem. Soc.*, **48**, 2893 (1926).

Miscellaneous. Palit and Dhar[37] have studied the influence of various nitrates on the rate of solution of mercury in nitric acid. Neville[38] has studied the rate of setting of plaster of Paris and of litharge-glycerine cements. In the former potassium salts are more effective accelerants than ammonium salts which are better than sodium, lithium and so on. Copper salts are better than magnesium salts. A definite lead compound is formed in the latter case. Lind and Bardwell[39] have continued their studies of actions initiated by α-particles. They show the elimination of hydrogen and methane from ethane, propane and butane, giving liquid and solid, saturated and unsaturated products. The last named are absent from the gas phase. They claim that the oxidation of methane and ethane occurs in one step but that this is not true of propane and butane. They also show reaction between methane and carbon dioxide.

Benton[40] has analyzed the available data on the kinetics of catalysed reactions in flow systems and has indicated one method of treatment of such systems for purposes of study of reaction kinetics.

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[36] *J. Am. Chem. Soc.*, **49**, 1460 (1927).
[37] *J. Phys. Chem.*, **30**, 1125 (1926).
[38] *J. Phys. Chem.*, **30**, 1037, 1181 (1926).
[39] *J. Am. Chem. Soc.*, **48**, 2335 (1926).
[40] *Ind. Eng. Chem.*, **19**, 494 (1927).

Chapter VII.

Photochemistry.

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The American literature in photochemistry continues to be sparse but several papers of the first importance have been published during the period now under review.

In the realm of technique, a paper by Cunliffe, Franklin, Maddison and Reeve[1] deals with the spectral intensities of mercury lamps under a variety of experimental conditions. Monochromatic technique is also detailed by Villars in a paper discussed subsequently in this review. The technique employed in photosensitised reactions employing excited mercury has also been extensively developed during the past year. Marshall[2] has devised methods of measuring the extent of absorption of $\lambda = 2536.7$Å. by a photosensitive system and has related this to the amount of reaction occurring. Dickinson and Mitchell[3] have devised a method of studying kinetically the mercury sensitised decomposition of ammonia at low pressures. The methods of producing intense sources of resonance radiation from cooled mercury arcs were outlined by Taylor[4] and an adaptation of one such arc to the study of photosensitised decomposition of a variety of compounds has been recorded by Taylor and Bates.[5]

The activity of excited mercury in various processes has been the object of study in these latter papers. Marshall[2] measured the quantum yields in the formation of hydrogen peroxide and formaldehyde and showed that from four to six molecules of product were formed per quantum of resonance energy, the computations being conservative and tending to yield minimum values.

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[1] *J. Phys. Chem.*, **30**, 1427 (1926).
[2] *J. Phys. Chem.*, **30**, 1078 (1926).
[3] *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).
[4] *J. Am. Chem. Soc.*, **48**, 2840 (1926).
[5] *Proc. Nat. Acad. Sci.*, **12**, 714 (1926)

A later paper[6] dealt with the kinetics of formaldehyde formation with indications that the rate was proportional to $[H_2]^{\frac{1}{2}} \cdot [CO]$ and therefore to the 3/2's power of the total pressure. Unpublished experiments by Whitten and Taylor have not confirmed this conclusion at pressures greater than atmospheric pressure and further work is needed in this problem. The ammonia decomposition studied by Dickinson and Mitchell[3] has shown that this is sensitised to $\lambda = 2536.7$Å. by mercury. The extension of the work by Mitchell and Dickinson[7] has shown that foreign gases such as argon and nitrogen do not influence the rate of decomposition but that hydrogen retards the decomposition markedly. The authors set up a mechanism for this and hence deduce the very interesting conclusion that collisions of the second kind between mercury and ammonia are only four % as frequent as those between mercury and hydrogen. Their work cannot be regarded as final since, as has been shown by Taylor and Bates,[5] the initial products of both the photochemical and the photosensitised decomposition contain hydrogen greatly in excess of the stoichiometric concentration. This points to a stepwise decomposition of ammonia; the inhibiting influence of hydrogen may be in part concerned with this.

A most important contribution to the hydrogen-chlorine reaction is due to Porter, Bardwell and Lind.[8] They have demonstrated a perfect parallelism between the sensitivity of such gas mixtures to α-particles on the one hand and to light on the other. Whatever mechanism is devised for the one must therefore be applicable to the other in so far as it explains the abnormal yield per quantum in the process, though the initial process in the activation may differ in the two cases. This research also would suggest that the ideas of Rice[9] as to the possible intervention of dust particles in the deviations from the law of the photochemical equivalent cannot be applied to this reaction, since the ionisation due to the α-particle would normally occur even in the absence of dust.

The reactions deviating abnormally from the equivalence law have been increased in number by the work of Bäckström[10] on the chain-reaction theory of negative catalysis, an investigation which constitutes a fundamental advance towards an understanding of this problem. Bäckström shows that the oxidation of several adehydes and of sodium sulfite solutions are reactions in which as many as 10,000-50,000 molecules react per quantum of incident energy. Both monochromatic and polychromatic light were studied. This result is all the more extraordinary in the light of the fact that in the case of sodium sulfite the oxidation occurs in dilute solution. The photochemist has a useful service to perform for chemistry in general in elucidating the mechanism of such extraordinary activations by a single quantum. The explanation will probably be transferable to ordinary nonphoto reactions such as explosions. On this view, inhibitors act by breaking reaction chains; how, one does not yet know.

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[6] *J. Phys. Chem.*, **30**, 1634 (1926).
[7] *J. Am. Chem. Soc.*, **49**, 1478 (1927).
[8] *J. Am. Chem. Soc.*, **48**, 2603 (1926).
[9] *J. Am. Chem. Soc.*, **48**, 2099 (1926).
[10] *J. Am. Chem. Soc.*, **49**, 1460 (1927).

There have been a number of studies of photodecompositions. Morgan and Crist [11] have subjected the decomposition of potassium persulfate to a thorough kinetic and photochemical study. Villars [12] has restudied the photolysis of potassium nitrate to potassium nitrite in solution and has corrected the erroneous conclusions of Anderson.[13] Villars' studies were conducted with monochromatic light and showed a decomposition of potassium nitrate per absorbed quantum dependent on the wave length and the pH of the solution. The efficiency increases with this latter up to $pH = 9.9$. Fasel and Karrer [14] suggest that collisions of the second kind between excited NO_2 molecules and N_2O_5 molecules are important in the photodecomposition of the latter. This problem, however, is still very much a matter for further investigation. Forbes and Leighton [15] have discussed the possible causes for a small increase in yield on electrolysis of dichromic acid when illuminated.

A correction has been made by Kistiakowsky [16] of some errors in an earlier investigation by Rideal and Williams [17] on the photochemical stationary state induced by the action of light on the equilibrium system ferrous-ferric iron; iodine-iodide. This example now forms a good case, suitable for instructional purposes, to exemplify both the stationary state and the law of the photochemical equivalent. The technique is simple and rapid and the quantum yield is unity over a wide range of frequencies.

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[11] *J. Am. Chem. Soc.*, **49**, 16, 338, 960 (1927).
[12] *J. Am. Chem. Soc.*, **49**, 326 (1927).
[13] *J. Am. Chem. Soc.*, **46**, 797 (1924).
[14] *J. Am. Chem. Soc.*, **48**, 2837 (1926).
[15] *J. Phys. Chem.*, **30**, 1628 (1926).
[16] *J. Am. Chem. Soc.*, **49**, 976 (1927).
[17] *J. Chem. Soc.*, **127**, 258 (1925).

Chapter VIII.

Determination of Crystal Structure by X-Rays.

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Much has been learned of the internal structure of solids since the first X-ray diffraction experiments of fifteen years ago. In this time methods have been developed for obtaining and identifying the diffraction effects from single crystals and from both completely disordered and partially oriented aggregates of crystals. By combining the results of mathematical crystallography with what has been ascertained of the laws of X-ray reflection, procedures have been formulated which often lead to the undoubtedly correct arrangement of the atoms in crystals. In less favorable instances these same modes of analysis furnish a sure knowledge of the correct space group and even of the general type of atomic arrangement. As a consequence of their use a more or less complete knowledge has been gained of the positions occupied by the atoms in several hundred crystals. The thoroughly and satisfactorily elucidated structures are, however, for the most part confined to relatively simple chemical substances possessed of a high degree of crystal symmetry. These experimental results provide a good picture of the way in which atoms are bound together in most simple inorganic solids. At the same time they lead to a certain, though as yet most imperfect, idea of the factors which determine the atomic array in such crystals.

Most crystals, including those possessed of the greatest interest both to the chemist and to the crystallographer, are much too complicated to permit of complete analysis by existing information. It is therefore the essential problem of crystal analysis at the present time so to amplify the existing methods of study that the atomic arrangements in these more complex crystals may be found with as much assurance as now attends investigations of the structures of simpler type.

Crystal analysis will develop through the introduction of new methods of interpretation or by reason of an increased and more accurate understanding of the laws governing X-ray reflection. It will likewise grow through the study of new sorts of crystals which are interesting either for the light that they throw on chemical problems or because a knowledge of their structure can be made to contribute towards an understanding of more complex crystals. For the purposes of the present review it is convenient to treat American contributions to crystal analysis during the last two years under the two heads of (1) methods and (2) results. A bibliography of pertinent American publications is appended to this chapter. When it is desirable to discuss papers not of American origin, their references are to be found in foot-notes.

Methods of Crystal Analysis. At present an accurate calculation cannot be made of the intensities of reflections from planes in a crystal of known atomic arrangement. This is mainly due to an incapacity to provide a satisfactory evaluation of the scattering powers of atoms for X-rays. Since the development of atomic theory is not such that satisfactory theoretical deduction of the intensity of reflection is likely to be soon forthcoming, the development of crystal analysis demands recourse to direct and detailed experimentation.

Several years ago an accurate measurement ([a]) was made of the intensities of a few X-ray reflections from single crystals of rock salt. Following the theoretical discussion of Darwin ([b]) for imperfect crystals, the results of these intensity measurements were expressed by grouping together in the form of an "F-curve" those imperfectly known factors which depend upon the atomic structure. It is of the utmost importance to obtain experimental determinations of the F-curves, or their equivalents, through the accurate study of many kinds of crystals. This can obviously only be done satisfactorily for crystals of completely known structure. From many F-curves of various atoms established in this way it can be ascertained whether the F-curve of an atom is the same in all the crystals in which it occurs.

Although no extensive program of this sort has been actively pursued, most of the F-curves that have been determined during the last two years have been made in this country. The intensities of several reflections from single crystals of fluorite (51)† have been measured. The F-curves of the atoms in lithium, sodium and calcium fluorides, in sodium chloride (37, 32, 40, 29, 4) and in metallic aluminum (4) have been established from studies of the intensities of powder reflections. Accurate observations have been made bearing on the important question of the influence of crystal size (33, 37) upon intensity and some data have been collected concerning X-ray absorption (34) in crystals. These data and the similar results of workers (c) in other countries add much to our knowledge of the intensity of X-ray reflection. It must be emphasized, however, that such measurements are needed from very many crystals of known structures before F-curve data can safely be used in studies of the atomic arrangement in more complex crystals.

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[a] Bragg, James, and Bosanquet, *Phil. Mag.*, **41**, 309 (1921).
[b] *Phil. Mag.*, **27**, 315 (1914).

Many measurements upon alkali halides were obtained to test the application (23) of a Fourier analysis of all of the diffraction data provided by a crystal. From the details of this analysis its atomic arrangement is deduced. This procedure was reached through a theory of X-ray diffraction built upon quantum principles. Though never actually used, the possibility of making such an analysis of the diffraction intensities from crystals was suggested (d) long ago. It has recently been shown (11) that this mode of analysis does not arise uniquely from quantum ideas but can equally well be deduced from classical pictures of X-ray diffraction. As applied to several simple halides (31, 38, 39) this Fourier analysis gives the known atomic distributions. For the diamond (39) it yields distributions which may or may not possess physical reality. The most rigorous test to which it has yet been subjected is its deduction of the structure of the tetragonal mercurous halides (35). The atomic arrangement thus found is in complete accord with that obtained through the usual methods. It is difficult to know how useful Fourier analysis will prove to be for practical studies of crystal structure. It is a serious disadvantage that its successful application requires in many cases an approximate knowledge of the atomic arrangement. This procedure makes a simultaneous use of intensity data from all of the important reflections from a crystal. Though at the present time this is a hindrance to its best application it may in the future make it very useful in establishing the precise atomic positions once their approximate arrangements have been found by other methods.

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† Superior numbers refer to bibliography at end of chapter.

[c] Barth, *Z. Physik*, **40**, 804 (1926); James and Randall, *Phil. Mag.*, **1**, 1202 (1926).

[d] Bragg, *Phil. Trans. Roy. Soc.*, **215A**, 253 (1915).

Two American books dealing with X-rays have been published in the last two years. One of these, by G. L. Clark, is entitled "Applied X-rays." As its title suggests it is devoted primarily to topics which do not lie within the scope of this report. Nevertheless it contains chapters describing very briefly some of the methods and results of crystal structure study. The other book, "X-rays and Electrons," by A. H. Compton contains perhaps the best available discussion of the intensity of X-ray reflection by crystals. Methods and results of crystal analysis are described in a series of papers (14, 15, 16). A critical summary of the existing structure data (81) is published in Volume I of the International Critical Tables.

Several papers recount changes in apparatus for crystal analysis. Thus the outfit sold commercially for preparing powder photographs has been adapted (9) to the making of the pin-hole photographs useful in investigating crystal orientation in worked metals. A modified powder spectrograph (10a) and the details of a spectrometer outfit (10) have been described. A focusing powder spectrograph (45) of the Seeman-Bohlin type has been designed for work at low temperatures. Calculations have been published for ruling the usual gnomonic protractor (48a) for Laue photographs in terms of sines of reflection angles instead of distances on the photographic plate. The simple cam device which has for many years been used for crystal rotation in spectrographic observations has received (26) a detailed discussion. A way of making space models (90) for more complicated crystal structures has also been outlined.

The Results of Crystal Analysis. It is impossible to discuss the results of studies of the structures of crystals without taking into consideration their relation to the two radically different schools of crystal analysis which now exist. One of these groups of investigators, which in its thought and procedures is largely dominated by the Braggs in England, seeks to obtain structures for complicated crystals. To this end it is assumed that the "atomic sizes" which are found to prevail in various of the simpler crystals are the essential factors in determining the atomic arrangements in more complicated ones. It is also considered that the intensities of X-ray reflection by different kinds of atoms are given with a considerable degree of accuracy by F-curves calculated ([e]) from a form of the Bohr theory of the atomic structure. The atomic arrangements arrived at in this way are possible rather than necessarily correct ones. Those who follow this school of thought have that advantage which follows from the fact that they are immediately engrossed with the more interesting chemical compounds which are an ultimate goal of all crystal analysis. Their results, however, suffer from the disadvantage that usually there is no immediate way of telling whether they are correct. In contrast with this mode of approach there is that of the group which was originally formed around the use of the theory of space groups in crystal analysis. It is the essential thesis of this group that sound knowledge of the structures of crystals will be more rapidly and surely achieved by pursuing crystal analyses only as far as they yield results which can be shown to be necessarily correct. From this standpoint the range of the substances amenable to attack is gradually extended through improvements in the methods of crystal analysis and through developments in our knowledge of the laws governing the phenomena of X-ray reflection. A majority of the crystal structure investigations recently published in America adhere more or less closely to this second point of view.

Studies upon metals have been devoted for the most part to more accurate determinations of the sizes of unit cells. Powder measurements have furnished a very accurate determination ([5]) of the size of the unit cube of alpha-iron. Similar data have led to more accurate spacings for tungsten ([13, 18, 19, 20]) and a number of other metals. Better diffraction measurements ([45]) from metallic potassium have resulted from photographs taken at a reduced temperature. Chromium ([68]) electrodes deposited under various conditions always proved to have the usual atomic arrangement. Powder photographs of metallic zinc ([24, 67, 64]) taken at various temperatures up to its melting point show that no structural dimorphism exists.

It has been found that certain films of nickel sputtered in hydrogen are not ferromagnetic. Their preliminary X-ray examination ([49]) was thought to show that they were amorphous. Additional experiments ([50]) upon them and upon similar films of cobalt and iron sputtered in helium give evidence of a pattern like that of the crystalline metal but expanded by from 6 to 20%. These surprising results are not yet sufficient to prove whether

[e] Hartree, *Phil. Mag.*, **50**, 289 (1925).

this corresponds to an actual swelling of the metal structure or to the formation of a compound with the sputtering gas. All of these films, when heated to 350°C., become magnetic and show the usual diffraction pattern of the metal.

Two inter-metallic compounds have been investigated. One of these, magnesium plumbide, $MgPb_2$, ([27]) has the calcium fluoride structure. Magnesium dizincide, $MgZn_2$, ([25]) is hexagonal with a new type of atomic arrangement. Powder photographs of alloys ([54]) of thallium and lead show the existence of solid solutions having the atomic arrangements characteristic of lead and of thallium. There is no evidence for the existence of compounds.

Powder photographs which, however, are incapable of establishing its atomic arrangement, have been made of solid oxygen ([53]). Similar data are published for solid carbon dioxide ([52]). As a consequence of an active discussion ([f]) of this structure during the last few years, fairly good agreement now exists between the atomic arrangements found by different investigators.

Reflection measurements ([62]) from cleavage faces of crystals of the beta form of aluminum oxide show it to have the longest spacing thus far found for an inorganic crystal. Laue photographs, together with these spectral data, have been used ([44]) to define the unit cell and the space group of this crystal. Its atomic arrangement proves to be too complicated for study by existing methods. Several investigations have in the past been carried out upon the two tetragonal modifications of TiO_2—rutile and anatase. Laue data have not been published from rutile and a thoroughly satisfactory study has not been made of anatase. It has recently been stated ([46]) that the Laue data from these two crystals agree with their published structures. In the high temperature modification of quartz ([77, 79, 80]) the oxygen atoms form regular tetrahedrons about the silicon atoms in such a way that each oxygen atom is equidistant from two silicon atoms ([g]). Ferrous oxide ([83]) proves to have a sodium chloride arrangement of its atoms.

Of considerable chemical interest are determinations of the atomic positions in crystals ([43]) of sodium and potassium trinitride and of potassium cyanate. They show that the trinitride group in these substances must have a chain rather than a ring-like configuration. The X-ray data from potassium cyanate are scarcely to be distinguished from those of the trinitride. Accurate spacing measurements have been recorded from a number of solid solutions of silver halides (76). A detailed investigation of the structure of the mercurous halides (36, 35) seems to show (h) the existence of molecules having the composition Hl-Hg-Hg-Hl. Earlier experimental results upon CsI_3 have been shown to be erroneous and correct (8) unit cells and space groups have been established for this crystal and for $CsBr_2I$. The atomic arrangements are too complicated for present analysis. The space group of mercuric iodide (30) and its unit cell have been deduced (i) from powder photographs and from spectrometer measurements upon single crystals. Crystals of cesium fluogermanate (95) and of ammonium chloroplumbate (86) have the ammonium chloroplatinate structure. The atomic arrangement has been found in the true coordination (91) compound (j) $(Co\cdot 6NH_3)I_3$. The six ammonia molecules are distributed in exactly the same way about the central cobalt atom as they are about the nickel atom in the ammoniate, $NiCl_2\cdot 6NH_3$. The general marshalling (96) of the atoms in $(Co\cdot 6NH_3)(ClO_4)_3$ is the same as that of the corresponding atoms in the iodide. But the structure contains too many variable parameters for an exact determination of atomic positions. It is interesting to find that the atoms and the atomic groups (93) in Na_2CaSiO_4 have the same distributions as atoms and groups in this iodide and perchlorate.

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[f] DeSmedt and Keesom, *Z. Krist.*, **62**, 312 (1925); Mark and Pohland, *Z. Krist.*, **61**, 293 (1925); **64**, 113 (1926).

[g] Bragg, *J. Soc. Glass Tech.*, **9**, 272 (1925); Bragg and Gibbs, *Proc. Roy. Soc.*, **109A**, 405 (1925); Gibbs *Proc. Roy. Soc.*, **107A**, 561 (1925).

Crystals of sodium periodate (21), $NaIO_4$, have the same atomic arrangement (k) which has previously been suggested for the minerals scheelite, $CaWO_4$, and wulfenite, $PbMoO_4$. In all of these crystals the oxygen atoms are tetrahedrally arranged about a central atom of iodine, tungsten or molybdenum. Two American determinations (63, 92a) of the space group of barium sulfate correct an earlier erroneous investigation and agree with one another and with the results of three European (m) studies. Diffraction data from crystals (7) of magnesium cyano-platinite heptahydrate, $MgPt(CN)_4\cdot 7H_2O$, lead to a unit cell of most unusual shape. The study of this crystal could not be carried beyond a determination of its probable space group. Silver ortho-

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[h] Hylleraas, *Physik. Z.*, **26**, 811 (1925); Mark and Steinbach, *Z. Krist.*, **64**, 79 (1926).

[i] Bijvoet, Claassen and Karssen, *Proc. Roy. Acad. Sci.*, Amsterdam **29**, 529 (1926).

[j] Hentschel and Rinne, *Ber. Sachs. Akad. Wiss. Leipzig*, **79**, 1 (1927).

[k] Hylleraas, *Z. Physik.*, **39**, 308 (1926).

[m] Basche and Mark, *Z. Krist.*, **64**, 1 (1926); James and Wood, *Proc. Roy. Soc.*, **109A**, 598 (1925); *Mem. Proc. Manchester Lit. Phil. Soc.*, **96**, Session 1924-25; Rinne, Hentschel and Schiebold, *Z. Krist.*, **64**, 164 (1925).

phosphate (78) and the corresponding arsenate have a new type of crystal structure. The oxygen atoms are grouped about the phosphorus or arsenic atoms so as to form regular tetrahedrons. Aluminum metaphosphate has cubic symmetry. An attempt (97) to determine its atomic arrangement led to the surprising result that the structure of this chemically simple compound is one of extreme complexity.

A study (n) of pentaerythritol made several years ago appeared to prove that a tetrahedral distribution of the valencies about its central carbon atom is impossible. Confirmatory Laue data (42) were published but apparently better results (o) indicate a crystal symmetry lower than that previously found. A space group determination (41) upon the cubic crystals of β-benzene hydrochloride and hydrobromide shows that the molecules do not possess a six-fold axis of symmetry but rather have a three-fold axis combined with a center of symmetry. Tetramethylammonium chloroplatinate (47) has the same type of atomic arrangement as ammonium chloroplatinate, with methyl groups tetrahedrally arranged around a central nitrogen atom.

Existing determinations permit of a more or less satisfactory picture of the structural relationships prevailing in many of the salts composed of strongly electropositive and strongly electronegative atoms. The few thorough analyses that have been made of molecular compounds likewise indicate the spacial existence of the usual chemical molecules. Little sound knowledge yet exists of the structure of crystals built up essentially of amphoteric atoms. Among such crystals the silicates constitute the most numerous group. Unfortunately most silicates are both chemically and crystallographically so complex that little real progress can now be made in the elucidation of their structures. Nevertheless arrangements based upon some experimental data have been suggested (p) for several more or less complex crystals of this type. It is scarcely possible to know how nearly these determinations give true pictures of the prevailing atomic arrangements. Though some of the simplifying assumptions upon which they are based are frequently maintained, existing data indicate that at best they are often not more than approximately maintained.

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[n] Mark and Weissenberg, *Z. Physik.*, **17**, 301 (1923).

[o] Nitta, *Bull. Chem. Soc. Japan*, **1**, 62 (1926).

[p] Bragg and Brown, *Z. Krist.*, **63**, 122, 538 (1926); *Proc. Roy. Soc.*, **110A**, 34 (1926); Bragg and West, *Proc. Roy. Soc.*, **111A**, 691 (1926); *ibid.*, **114A**, 449 (1927); Bragg, *ibid.*, **113A**, 642 (1927).

Other X-ray observations that have been made upon silicates bespeak the danger that may arise from the application of simplifying the analyses of these crystals. Thus it is hard to explain on the basis of any simple idea of a close packing of large oxygen atoms why the two compounds $Al_2O_3 \cdot SiO_2$ (as sillimanite) and $3Al_2O_3 . 2SiO_2$, mullite, give X-ray diffractions (56, 57, 59, 88) scarcely (q) to be distinguished from one another. It is equally difficult to form a picture of simple spacial distributions which will cause Na_2CaSiO_4 and $Na_4Ca(SiO_3)_3$ to give almost identical diffraction patterns (93).

These two years have seen the last of the numerous discussions and experiments which have finally established the Compton-Debye wave length shift. These same and other experiments (1, 3, 8, 22) appear likewise to have disproved the existence of tertiary radiation, of characteristic reflections of X-rays through crystalline reflection and of other anomalous reflection phenomena.

Besides the studies which were carried out primarily to ascertain atomic positions within crystals, diffraction data have been used to identify crystalline phases. Thus it is found that the substances (57) called vaterite and μ-$CaCO_3$ give identical reflections (r) and constitute a modification of calcium carbonate different from either calcite or aragonite. Powder photographs have also been used to classify the pyroxene minerals (92) according to their structural types and to follow the decomposition through heating of the mineral dumortierite (84). Similar photographs have likewise been examined from several sulfide minerals (66). A puzzling problem (71, 72, 73, 74, 75) is introduced by the identification of a substance (a magnetic form of Fe_2O_3) giving an X-ray pattern indistinguishable from that of magnetite. Examination (65) of the relative widths of the powder lines of alpha- and of meta-stannic acids indicates that the crystals in both have the same atomic arrangement as cassiterite but that those in the meta-preparations are the larger. By using X-rays of different wave lengths, and hence of different penetrating powers, for the preparation (6) of powder photographs of a layer of rust-resisting oxide on iron, this layer is found to consist of three films—FeO nearest the metal, next some Fe_3O_4, and finally an outside coating of Fe_2O_3. X-ray diffraction measurements have been used to investigate the solid phases present in certain catalysts and to gain

[q] Mark and Rosbaud, *Neu. Jahrb. Miner.*, **54**, 127 (1926); Rosbaud, *Z. Elektrochem.*, **32**, 317 (1926).

[r] Rinne, *Z. Krist.*, **60**, 55 (1924); Heide, *Centr. Min.*, **1924**, 641.

some idea of the sizes of the crystals composing them. Several nickel catalysts ([10a]) and some of the iron catalysts ([85]) used for ammonia synthesis have thus been studied.

In Europe much attention has been given to the X-ray diffractions from the fatty acids and other long chain carbon compounds. Americans have not taken a very active interest in this field of investigation. It was at first supposed that the large spacings observed from solid films of these compounds were direct measures of the lengths of their carbon chains. It was imagined that under the conditions of preparation of these films they were not truly crystalline. By some they were said to be in a semi-crystalline state which had previously been described as "smectic." Optical examination ([89]) of these films as ordinarily prepared, as well as the growth of single typical crystal specimens ([s]), proves that they are genuinely crystalline. The low symmetry of at least most of these substances is such that the observed long spacings do not directly measure the length of their molecular chain.

Measurements ([70]) have been made of the diffraction patterns produced by several organic liquids. Many soda-lime-silica glasses ([94]) have been photographed. The character of the pattern obtained is related to the composition of the glass but insufficient work has been done to trace this connection.

The gradual accumulation of knowledge of the structure of crystals has led to a variety of speculations concerning the laws determining atomic arrangement in crystals. Much attention has been given for several years to the idea that in crystals more or less spherical atoms are packed together. There have been American contributions ([17, 48b]) to discussions of the sizes of such atoms. A recent paper reverts to calculations based upon cubical and polyhedral atoms. Attempts have been continued to relate ([48]) the different types of structures for simple salts and the intimate details of bonds assumed to exist between their atoms. A number of foreign papers have been devoted to lengthy discussions of relationships between the relative sizes ([t]) of the atoms in crystals or the forces ([u]) between these atoms, and their spacial arrangements. These ideas have recently been discussed ([61]) in terms of the current form of atomic theory. Sound correlations between the atomic properties of the elements constituting a crystal and its structure will undoubtedly finally be established in some such way as that outlined in these latter papers but it is impossible to know how much of lasting value attaches to the details of current treatments.

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[s] Gibbs, *J. Chem. Soc.*, **125**, **2622** (**1924**).

[t] Goldschmidt, *Vid. Akad. Skr. I* (*Mat. Nat. Kl.*), 1926; No. 2; *Ber.*, **60**, **1263** (1927).

[u] Hund, *Z. Physik.*, **34**, **833** (**1925**); *Physik. Z.*, **26**, **811** (**1925**).

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Chapter IX.

X-Ray Examination of Materials.

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There are three types of X-ray examination of materials, one concerned with gross structure or radiography, the second with fine structure as deduced from characteristic diffraction of X-rays by substances, particularly crystals, and the third with spectroscopic study of materials used as targets in X-ray tubes, or as absorbing screens.

Radiography. Depending upon the fact that X-rays penetrate matter opaque to light, and that they are differentially absorbed depending upon the density of a material, "shadowgraphs" of non-homogeneous materials may be obtained photographically or observed on fluorescent screens. The oldest and still most important application is medical diagnosis. The experimental technique is comparatively simple so that progress in America during the past year has been directed principally along the following lines:

1. Improved X-ray constant potential power plants[1] for better definition in radiographs, particularly for soft tissue diagnosis.[2]

2. Research on design and construction of X-ray tubes capable of withstanding 300,000 volts and higher, and thus of producing rays which will penetrate greater thicknesses of materials (four inches of steel now the limit).

3. Application of absorbing chemical compounds to define areas under examination; this is particularly true in medical diagnosis by injection and concentration of lipidiol (iodized oil), tetraiodophenolphthalein,[3] etc., in organs.

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[1] For example, Mutscheller, *Am. J. Roentgenology and Radium Therapy*, **17**, March, 1927.

[2] *Cf.* all numbers of *Am. J. Roentgenology and Radium Therapy* and *Am. J. Radiology*.

[3] Newell, *Am. J. Roentgenology and Radium Therapy*, **17**, 443 (1927).

4. Design of portable radiographic plant for industrial purposes.[4]

5. The use of the photographic densitometer for determining, from the photographic blackening, the size of an internal defect or inhomogeneity in the direction normal to the film.[5]

6. New applications of radiography in chemistry and technology. Routine testing is coming into more general usage but on account of expense the chief usefulness is in developing a technique of producing sound materials.

a. Steel castings for internal gas cavities, sand and slag inclusions, pipe cavities, porosity, cracks and metal segregations.[6] The detectability of defects in steel is now down to ½% in ¼ inch and 1% in 2 inches.

b. Welds,[7] including all-steel automobile bodies, for soundness.

c. Control of the coal-washing process and the classification of minerals.[8]

d. Some of the practical applications reported in the United States are: determination of symmetry of golf ball centers, adhesion of rubber to cords in tires, inspection of reclaimed rubber for nails and foreign matter, inspection of insulated wire, inspection of filling of grenades and shells, inspection of wood used in airplanes for worm-holes, cracks and knots, inspection of walls for hidden wires and pipes, examination of packages for contraband (particularly in California), examination of size and location of desired holes in Swiss cheese (!).

e. In the chemical laboratory, the measurement of internal diameters of metallic capillary tubes and the rise of liquids in these in determinations of surface tension.[9]

f. Examination of old paintings for retouching, superposed pictures, etc., and the partial identification of pigments from absorbing power for X-rays.[10]

The Examination of the Fine Structure of Materials. A. *Types of Information:* When an X-ray beam, defined by pinholes or slits, passes through or is reflected from a specimen, a diffraction pattern is obtained which may yield the following types of information: (1) Crystalline or amorphous. (2) Macrocrystalline or colloidal. (3) Lattice structure, atomic and molecular arrangement and dimensions for crystals; distances of nearest approach of molecules or aggregates of molecules acting as units in liquids, gels, etc. (4) Chemical identity (compound, mixture, adsorption complex); purity; phase structure; solid solution, etc. (5) Transformations and allotropic modifications. (6) Chemical change; ageing. (7) Single crystal or aggregate. (8) Random, or fibered aggregate. (9) Degree of fibering deformation; effect of fabrication: rupture, rolling, drawing, torsion, impact, complex deforming forces, electrodeposition, annealing, etc.; directional properties. (10) Quantitative analysis of the mechanism of deformation. (11) Grain size. (12) Internal strain. (13) Differentiation between surface and interior structure. (14) The effect of high and low temperatures, and high pressures, and the nature of recrystallization. (15) Uniformity of structure in different lots; in same lot; in same unit. (16) Differentiation between same materials, with satisfactory and unsatisfactory properties for given practical purpose.

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[4] St. John, *Ind. Eng. Chem.*, **19**, 339 (1927).
[5] Norton and Warren, *J. Optical Soc. Am.*, **13**, 525 (1926).
[6] *Proc. Am. Soc. Testing Materials*, **26**, pt. I, 581 (1926).
[7] Norton, *Iron Age*, **118**, 409 (1926).
[8] St. John, *Ind. Eng. Chem.*, **19**, 339 (1927).
[9] First tried by Owen and Dufton, *Proc. Phys. Soc.*, **38**, 204 (1926).
[10] Burroughs, *Atlantic Mo.*, **137**, 520 (1926), gives an excellent account of the premier investigations at Fogg Art Museum, Harvard University.

B. *Apparatus and Methods.* Clark, Brugmann and Aborn[11] have developed the technique and emphasized the monochromatic pinhole method as most useful for the examination of materials because of its simplicity, flexibility and production of diffraction patterns 360° in azimuth. They describe a new multiple diffraction apparatus (18 simultaneous exposures from one X-ray tube), combining the monochromatic pinhole (or Laue) and the powder diffraction methods. Davey[12] describes the modifications in the design of the familiar General Electric diffraction apparatus to include the pinhole method.

Clark, Brugmann and Kaufman[13] have designed an automatically adjustable specimen and photographic film holder to be used with pinholes for the study of surface reflections. Kunberger and Lanyon[14] in the writer's laboratory have constructed a choke coil for controlling filament current in X-ray tubes which is eminently satisfactory for apparatus in continuous operation, in contrast with the inherent weakness of the usual contact resistance. For small X-ray spectrographs, cameras, high-intensity X-ray tubes with interchangeable targets, etc., X-ray experimenters in the United States are still largely dependent upon importations from England or Germany, or upon special construction. A few of such specially designed and constructed spectographs and cameras have been described.[15]

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[11] *J. Optical Soc. Am.*, **12**, 379 (1926).
[12] *Gen. Elec. Rev.*, **29**, 127 (1926).
[13] Colloid Symposium Monograph, **4**, 159 (1926).
[14] *J. Optical Soc. Am.*, **13**, 243 (1926).

Bozorth[16] in an important paper presents a method for the analysis and measurement of the thickness of thin layers (in this case oxides of iron on iron), based on surface reflection of molybdenum, iron and copper rays. The iron and copper K_a rays penetrate the coating to different depths and give information about different parts of its structure. An automatic voltage regulator for a Hadding gas-discharge X-ray tube is also described. Horovitz[17] has designed a focussing vacuum spectrograph in which metallic films were deposited on glass by atomic rays and were then analyzed by X-rays directly. Deposits of metallic potassium at liquid air temperatures produced a body-centered cubic pattern if the films were at least 0.15 mm. thick.

C. Metals and Alloys. 1. *Examination for constitution and lattice arrangement.* While this subject properly comes under the head of determination of crystalline structures, mention will be made of a few American investigations of the past year which were designed to study the fundamental effects of certain practical metallurgical processes.

Sillers[18] has found no evidence in electrodeposited chromium of a new modification as reported by Bradley and Ollard in England. Miss F. H. Clark[19] used X-ray analysis in her comprehensive study of β-brass and found that quenched 60:40 metal gave a few faint lines of face-centered and body-centered lattices, and that quenched and reheated brass containing fine sorbitic structure also gave this mixed pattern. Bain[20] from X-ray studies of hardenable copper alloys containing silicon, nickel, cobalt and chromium was able to show that hardening of the alloy is due to slight lattice distortion produced by the absorption of alloying atoms, sufficient to oppose smooth slip on atomic planes. Bain and Griffiths[21] identified a new and complex constituent in alloys of iron, chromium and nickel at temperatures between 800 and 950°, and solid solutions above 1000° of austenite containing chro-

[15] For example, Norton, *J. Optical Soc. Am.*, 13, 231 (1926).
[16] *J. Am. Chem. Soc.*, 49, 969 (1927).
[17] *Proc. Am. Phys. Soc.*, 1, no. 12 (1926).
[18] *Trans. Am. Electrochem. Soc.*, 51, preprint (1927).
[19] *Am. Inst. Mining Met. Eng.*, No. 1630-E (1927).
[20] *Am. Inst. Mining Met. Eng.*, No. 1657-E (1927).
[21] *Am. Inst. Mining Met. Eng.*, No. 1850-C (1927).

mium and ferrite containing nickel. McMillan and Pauling[22] found in alloys of lead and thallium at room temperature no compounds but two solid solutions, one having the low temperature structure of thallium and the other of lead. Anderson[23] reports the results of investigations on duralumin with a lattice essentially unchanged from that of pure aluminum (slight contraction with 6% copper); the effects of cold work and heat treatment on the appearance of the crystal spectrum lines are discussed. Fink and Campbell,[24] in their studies of drastically quenched eutectoid and hypereutectoid steels, found evidence of a body-centered tetragonal structure which Bain considered to be an arrested stage in the allotropic change from γ- to α-iron. This important discovery has received very recent complete confirmation in the work of Selyakov in Russia.[25]

2. *Examination for grain orientation and effects of mechanical and heat treatment.* The incidental use of X-rays in determining the orientation of single metal crystalline wires and rods prior to mechanical and physical tests has been advocated and extended by McKeehan[26] in his studies of magnetism, twinning, etc. Thus far most of the theoretical and experimental work on the mechanism of plastic deformation and recrystallization of pure metals as deduced from X-ray results has been conducted in Germany, England and Japan. Much of this work has been tested in the United States[27] with the following conclusions concerning the direction of the fibering or deformation axis:

	Drawing	*Rolling*
Face-centered cubic metals	[111] [100]	[335], nearly [111]
Body-centered cubic metals	[110]	[110]

Reference should be made to the remarkable new results on recrystallization which show the persistence of preferred orientation after annealing, and the effects of small amounts of impurities. Copper when first hot-rolled, then cold-rolled and finally strongly annealed is characterized by orientation of cube edges in the direction of rolling, so that a sheet is obtained acting essentially like a single crystal and with mechanical properties altogether different from a sheet of small randomly oriented grains. X-ray studies have proved that 0.05% of iron in silver has a very great effect on recrystallization in preferred directions at room temperature and thus deleteriously affects silver plate unless copper is also present as impurity. By such fundamental studies the fabrication of metals is being reduced to a science.[28] Every impetus should be given to researches of this type in America.

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[22] *J. Am. Chem. Soc.*, **49**, 666 (1927).
[23] *J. Franklin Inst.*, **201**, 465 (1926).
[24] *Trans. Am. Soc. Steel Treating*, **9**, 717 (1926).
[25] *Nature*, **119**, 494 (1927).
[26] *Nature*, **119**, 705 (1927).
[27] For example, Norton and Warren, *Am. Inst. Mining Met. Eng.*, No. 1610-E (1927).

The problem of stresses in metals has received attention from both fundamental and practical standpoints. Lester and Aborn [29] have made a remarkably exhaustive and painstaking study of the behavior of iron crystals in steel under stress, involving 20,000 measurements of lines in powder diffraction spectra taken by the Hull method. It was found that the stress-strain relations for the crystals in the crystalline aggregates do not follow the smooth curves that characterize these relations for the aggregate. Hence, the crystals undergo strain recoveries by stepped slip, or small movements introducing no change in geometrical configuration, on application of increasing stresses to the aggregate; on removal of the load they may be left under stress, sometimes tension and sometimes compression, as measured by the actual displacements of the spectrum lines.

Clark, Aborn and Brugmann [30] have emphasized the practical significance of X-ray diffraction patterns with symmetrical intensity maxima lying on rings showing fibering or preferred orientation, and patterns with radial streaks indicating internal strain or distortion of the lattice planes. By standardization and comparison of these patterns they show that it is possible to develop a technique of fabrication of metals which will assure uniformity and desired properties. These researches at the Massachusetts Institute of Technology have been concerned in a practical way with the following metals:

a. Cast steel—original structure, effect of ordinary anneal, annealing conditions required for ideal structure without preferred directions or internal strain, plotting "isostrainal" lines in ordinary casting from X-ray data alone, derivation of suitable heat treatment to equalize these, etc.

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[28] For the most recent work *see* Schmid and Wasserman, *Z. Physik*, **40**, 451 (1926); Glocker and Widmann, *Z. Metallkunde*, **19**, 41 (1927); Sachs, *et al.*, *Z. Physik*, **41**, 889 (1927); **42**, 283 (1927).

[29] Army Ordnance, **6**, 120, 200, 283, 364 (1925-26).

[30] *J. Soc. Automotive Eng.*, **20**, 291 (1927); Clark, *Paper Trade J.*, **84**, No. 16, 47 (1927).

b. Cast steel test bars pulled at various temperatures from −100° to 1600° F.—showing distribution and mechanism of plastic deformation, location of blue brittle range, and extent of fibering.

c. Welds—comparison of metal structure (strain, grain-size) in various parts of ordinary arc and General Electric hydrogen atmosphere welds, the latter representing a self-annealed and ductile structure.

d. Sheet steel—comparison of hot and cold rolling and annealing, uniformity in different lots, same lot and same sheet, effect on X-ray pattern and identification of direction of last pass through rolls.

e. Forming steel—differentiation between satisfactory and unsatisfactory sheets, before and after forming, classification and identification of commercial grades from "dead soft" to "extra hard."

f. Steel wire—identification of the cause of die-cutting.

g. Case-hardened steel—identification of structure and effects of impurities; grain size and distortion.

h. Electric steel—correlation of diffraction patterns with magnetic hysteresis loss and control of heat treatment by X-ray patterns alone.

i. Aluminum alloys—ageing, tendency to intercrystalline corrosion.

j. Brass—cast and cold-rolled structures; season cracking.

k. Platinum and aluminum—effect of fine structure when used as deposition electrodes.

l. Copper—differentiation between metal corrosive or noncorrosive in ammoniacal liquors.

In the study by Russell and White[31] of the effect of oxygen concentration on the corrosion of copper by non-oxidizing acids, and in that by Russell, Chappell and White[32] on the effect of velocity on corrosion of steel under water, the metal specimens were subjected to X-ray analysis in the writer's laboratory as an aid to interpretation of the results on corrosion.

3. *Electrodeposited metals.* Following the earlier studies of Clark and Frölich on electrodeposited nickel, Frölich, Clark and

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[31] *Ind. Eng. Chem.*, 19, 116 (1927).
[32] *Ind. Eng. Chem.*, 19, 65 (1927).

Aborn[33] have made an X-ray investigation of lead electrodeposited under a very wide range of conditions, and have thus discovered the method of producing the most uniform and firmly adhering films for commercial purposes. These studies demonstrated the structure of lead dendrites, the orientation of grain on the electrode, and the remarkable effects of traces of gelatin and related addition agents in reducing grain size.

D. *Crystalline Inorganic Materials.* Most of the work on inorganic substances has been devoted to the investigation of the crystal structures of pure compounds (see Chapter VIII). Miss Farnsworth, working in the writer's laboratory, made an extended X-ray study of limes having different plasticities.[34] The calcium oxide samples which give plastic hydrates produce only the diffraction pattern for pure CaO, and the plastic hydrates give an hexagonal pattern with axial ratio 1.40. The patterns of the less plastic samples are complicated by additional lines of $Ca(OH)_2$ in the first case, and of $Ca(OH)_2$ and $CaCO_3$ in the second, the intensity of these lines being a measure, inversely, of plasticity. High temperatures and vacuum burning are conducive to greater plasticity. Azbe[35] has applied the results of X-ray crystal structure studies to the practical problems of lime-burning in a manner which promises much for further application of X-rays in the industry. At the Bureau of Standards[36] portland cement in all its phases is being subjected to X-ray investigation starting with the compounds CaO, $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3, $Ca(OH)_2$, $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$.

Bozorth,[16] as already indicated, has analyzed with X-rays the Bower-Barff protective coating, produced by the action of steam on iron at 700° with subsequent cooling in air, and identified layers of ferrous oxide, magnetite and ferric oxide in order, with respective thicknesses of 10^{-2}, 2×10^{-4} and 2×10^{-5} cm.

Miller[37] has been able to prepare an insoluble α-modification of germanium dioxide which gave an entirely different pattern (unanalyzed) than the ordinary form. The studies of Wyckoff and Morey[38] on the system soda-lime-silica parallel in one sense the studies of the ceramic materials mullite and sillimanite which gave practically identical patterns. Thus Na_2CaSiO_4, Na_4Ca-

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[33] *Trans. Am. Electrochem. Soc.*, 49, 369 (1926); *Z. Elektrochem.*, 32, 295 (1926).
[34] *Ind. Eng. Chem.*, 19, 583 (1927).
[35] *Ind. Eng. Chem.*, 19, 600 (1927).
[36] *Proc. Am. Phys. Soc.*, 1, No. 12 (1926).
[37] *Proc. Am. Phil. Soc.*, 65, 193 (1926).
[38] *Am. J. Sci.*, 12, 419 (1926).

$(SiO_3)_3$ and $Na_2Ca_2(SiO_3)_3$ all give very similar patterns in which the strong lines all coincide, while the differences lie in additional weak lines.

St. John[39] reports that he has found X-ray evidence of two forms of carbon stable at 2400°C. There is a growing application of X-rays to the identification of minerals. Clark, Aborn and Brugmann[30] announce, preliminary to detailed publication, the remarkable differences in the X-ray patterns from various types of asbestos, and the changes in these as the asbestos is chemically treated (acid, heat, etc.). Only one kind of asbestos is suitable as a base for catalysts and its purchase for this purpose may be made upon the basis of a single X-ray test diffraction photograph.

Farnsworth[40] has applied the X-ray method also to investigation of the cause of loss of tensile strength of plaster of Paris molds after recalcination. The particle size indicated in these patterns was definitely larger the smaller the tensile strength. The addition of ¼% Al_2O_3 prevented increase in particle size with successive reheatings and thus also the decrease in tensile strength.

E. *Crystalline Organic Compounds.* Most of the pioneer work in the field of applying X-ray diffraction methods to organic chemistry has been carried on in the laboratories of Bragg in England and deBroglie in France. This has been along the lines of unique analyses of single crystals, the interpretation of stereoisomerism, molecular symmetry, optical activity, the orientation, length, and polymorphic forms of long chain compounds in thin films, and the analysis of natural materials.

Clark[41] has studied paraffin waxes and observed that these mixtures give diffraction lines for only one hydrocarbon. The spacings corresponding to chain lengths vary depending upon the rate of cooling, and impurities for any given commercial wax. Clark, Aborn and Brugmann[30] have determined the conditions which are advantageous for molecular orientation of long-chain compounds (nature of backing, thickness of film, time in fluid state), and applied these observations to the case of lubricants. The soaps and glycerides in linseed and china wood oils have been studied also.

Mention should be made here also of the excellent paper by

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[39] *Ind. Eng. Chem.*, 19, 339 (1927).
[40] *Ind. Eng. Chem.*, 19, 714 (1927).
[41] *Nature*, 120, 12 (1927).

Hendricks and Bilicke[42] on the derivation of the molecular symmetry of β-benzene hexabromide and hexachloride.

Another interesting outgrowth of organic crystal analyses is the application of some of the long-chain compounds with large spacings as crystal gratings for the measurement of very long wave-lengths. In this way Dauvillier in France[43] was able to bridge the spectral gap from 20 to 136 A. U. using lead melissate (spacing 87.5 A. U.) as grating. Hunt[44] in the Bureau of Standards has verified and improved some of these measurements.

F. *Colloidal and Amorphous Materials.* 1. *Catalysts.* Clark,[45] in continuing work on particle size of metal catalysts as related to the activity, finds from photometric measurements of line breadths that there is a definite relationship between decreasing particle size to an optimum size, with increasing activity. These investigations of catalysts are being continued in order to discover the effect of every possible variable. The earlier work on nickel catalysts has inspired the new and excellent X-ray studies of catalysts by Levi in Italy.

2. *Practical studies of colloidal particle size.* The above type of investigation can be applied with great value to the study of paints, pigments, and enamels. Clark[45] reports measurements on a series of samples of stannic oxide used in enamels in which the particle size varied from 10^{-3} to 5×10^{-7} cm. Clark and Brugmann measured the particle size of case-hardened steel (martensite and troostite) to be nearly 10^{-7} cm. By means of the surface reflection apparatus mentioned above they have also demonstrated the extreme fragmentation on the surface of cold-worked metals.

3. *Carbon black.* A continuous transition by heat treatment between an active charcoal with an X-ray pattern indicating as nearly the amorphous state as possible (one very ill-defined ring) and graphite (sharp, many-line crystal spectrum) has been observed by Clark and Alm.[46] They found that the change in X-ray pattern of the active carbon lags behind the change in physical and chemical properties to those of graphite. This is evidence of a paracrystalline state in which crystalline layers are still too few and distorted to produce definite interference maxima.

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[42] *J. Am. Chem. Soc.*, 48, 3007 (1926).
[43] *J. Phys. Radium*, 8, 1 (1927).
[44] *Proc. Am. Phys. Soc.*, 2, No. 3 (April, 1927).
[45] Colloid Symposium Monograph, 4, 157 (1926).
[46] Colloid Symposium Monograph, 4, 155 (1927).

4. *Rubber and allied substances.* The first published account of the fact that rubber when stretched produces a crystalline fiber diffraction pattern was by Katz. This fact had been observed by Clark, and the essential phenomena described by Katz, though not the details, have been confirmed by him[47] and by Hauser and Mark in Germany. Clark and Hauser and Mark agree that a unit rhombic cell containing $(C_5H_8)_8$ is indicated from X-ray data, and that upon stretching a lower polymer phase is forced out of a higher polymerized phase which is thereupon oriented for diffraction. Clark has reported the only results and calculations on balata and gutta percha which differ from each other and from rubber; both contain crystalline matter when unstretched while rubber ordinarily does not. Gelatin and glue in stretched condition also show an incipient crystal-like arrangement. The polymerization of shellac upon heating has been followed by X-ray photographs.

5. *Liquids and gels.* Great interest has been aroused recently in the interpretation of "amorphous" patterns consisting of two or three diffuse diffraction rings. It is now definitely established that these are indicative of the distance of nearest approach of molecules or aggregates acting as units. Stewart and Morrow[48] propose the term *cybotaxis* for this state, and they propose to apply the conception to osmosis and other phenomena. They present results on liquid primary normal alcohols which show two spacings, one corresponding to chain length and one (constant for all) to cross section, in every way analogous to results with the solid state. Clark[41] has discovered that polymerization, oxidation, photochemical action, and solvent swelling of gels in rubber, nitrocellulose, linseed oil, and china wood oil (liquid and dried films) are indicated in a remarkable way by these simple patterns. In the last two cases, overageing is accompanied by actual crystallization.

6. *Cellulose.* Clark, Freudenthal and Kulp[50] have subjected a long series of natural cellulose fibers and all types of rayon to X-ray investigation and found them all crystalline except diacetate rayon. For natural or regenerated cellulose the same lattice is indicated [rhombic $(C_6H_{10}O_5)_4$] but the degree of fibering varies

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[47] *Ind. Eng. Chem.*, **18**, 1131 (1926).

[48] *Proc. Nat. Acad. Sci.*, 13, 222 (1927).

[50] *Proc. Am. Assoc. Textile Chemist and Colorists*, 1926, 234; *Am. Dyestuff Reporter*, 15, 788 (1926); *Techn. Assoc. Papers*, 10, 63 (1927); *Paper Trade J.*, 84, No. 16, 47 (1927); Colloid Symposium Monograph, 4, 169 (1926).

widely from random in a viscose film to nearly perfect in ramie and flax. Tension on the fiber in rayon production has large effects upon the fibering, as disclosed by X-ray diffraction, and also upon important practical properties. Sponsler and Dore[51] have made a large contribution towards the unique solution of the actual structure and constitution of a cellulose fiber by combining adequate X-ray data with all other available information. Amylene oxide linkage and unit crystal cells tangential to an annular fiber are important features.

X-ray Spectroscopic Examination. Qualitative and quantitative analyses of unknown substances used as targets or absorbing screens by spectroscopic measurement of characteristic radiation wave-lengths and application of Moseley's law are now made as a matter of course in several laboratories. The outstanding published results are of course those concerned with the discovery of illinium, element 61, by Hopkins and associates.[52]

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[51] Colloid Symposium Monograph, **4**, 174 (1926).
[52] Survey of American Chemistry, **1**, 51, 71 (1927).

Chapter X.

Electro-Organic Chemistry.

Charles J. Brockman,
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General. C. J. Thatcher[1] very briefly reviewed the development of organic electrochemistry in the past twenty-five years as a part of the Symposium on the Progress of Electrochemistry commemorating the founding of the American Electrochemical Society in 1902.

A "Bibliography of Electro-Organic Chemistry," compiled by Max Knobel, C. J. Brockman, and the Research Information Service of the National Research Council, was published in mimeographed form by the National Research Council in December, 1926. There are 809 references listed alphabetically by authors' names with the exact original titles and journal citations. A good subject index is included.

"Electro-Organic Chemistry,"[2] by C. J. Brockman, gives a thorough review of this field of electrochemistry in an organized and systematical manner. It contains over 1200 references to the journal and patent literature with author, patent and subject indexes.

A process[3] has been patented for the combination in a divided cell of the oxidation of an organic compound in the anolyte with the simultaneous reduction of another organic compound in the catholyte, using catalysers to assist.

Conant has extended his previous work on the potential relations of oxidation-reduction systems of organic compounds, dealing almost entirely with irreversible reactions. The field has been excellently summarized in a paper "The Electrochemical Formulation of Irreversible Reduction and Oxidation of Organic Compounds,"[4] in which all previous work by himself and by others is discussed. The problem to be solved has been stated: "Qualitatively the idea of 'powerful' reducing agents and 'mild' reducing agents has long been in vogue. Is this concept sound? The problem is really this: Is the rate of an irreversible process governed by the free energy change involved? In other words, will the speed of reduction of a substance be a function of the oxidation-reduction potential of the reagent employed?" The problem is too large to warrant complete discussion in so limited a space.

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[1] *Trans. Am. Electrochem. Soc.*, 51, preprint (1927).
[2] New York, Wiley, 1926, 339 p.
[3] Thatcher, U. S. P. 1,544,357 (June 30, 1925).

The intense color of solutions of triphenylcarbinol and its derivatives in acetic acid or alcohol containing a mineral acid is generally considered to be due to the formation of the so-called halochromic salts. Most investigators now agree that the formation of these halochromic salts is expressed by the reversible equation: $Ar_3COH + HX \leftrightarrows (Ar_3C)^+ + X^- + H_2O$. It has long been recognized that the formal relationships of these halochromic salts to free radicals of the type Ar_3C- is that of an inorganic salt to a metal. Conant[5] has found that just as a metal in contact with a solution of its salt has a characteristic electromotive force, so a mixture of a free radical and the corresponding halochromic salt has a definite potential.

The investigation of the irreversible reduction of organic compounds has been continued in a study of the reduction potentials of azo dyes.[6] One of the most trying parts of this work was the preparation of the azo dyes in a form which was sufficiently pure for potential measurements.

The fourth paper[7] in this series is a study of the "apparent reduction potential" of unsaturated carbonyl compounds. A series of twenty-six compounds was studied in 0.2 molar hydrochloric acid-acetone solution at 24°, using a variety of reducing agents.

A calculation has now been made of the free energy of reduction of a series of quinones referred to the gaseous state.[8] It has been shown that the relation between the structure of chloro-substituted quinones or their corresponding hydroquinones, and the reduction potentials referred to the gaseous state is simpler than if a dilute solution is taken as the standard.

Another series of investigations in this oxidation-reduction problem has been started, *viz.*, the irreversible oxidation of organic compounds. The first paper[9] is a discussion of the oxidation of aminophenols by reagents of a definite potential. The relative rates of oxidation of these compounds by several reagents of different potentials are of the same order of magnitude as predicted by calculation from the electrochemical equations which have been developed. Some irreversible oxidations may be formulated in electrochemical terms by determining the rates of oxidation of each compound by each member of a graded series of reagents and then estimating the potential of the oxidizing agent which should just cause "appreciable oxidation." The potential of this hypothetical reagent (with an oxidizing power of one equivalent) is defined as the "apparent oxidation potential" of the substance under investigation.

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[4] Conant, *Chem. Rev.*, **3**, 1 (1926).
[5] Conant, Small and Taylor, *J. Am. Chem. Soc.*, **47**, 1959 (1925).
[6] Conant and Pratt, *J. Am. Chem. Soc.*, **48**, 2468 (1926).
[7] Conant and Lutz, *J. Am. Chem. Soc.*, **49**, 1083 (1927).
[8] Conant, *J. Am. Chem. Soc.*, **49**, 293 (1927).

In determining the apparent oxidation potential of certain phenols and enols[10] it has been found that the speed of irreversible oxidation of α-naphthol in an acid solution is related to the potential of the reagent used. In many cases the rate of oxidation is independent of the dilution, therefore it is suggested that a reversible formation of a free radical is followed by a monomolecular irreversible isomerization of the free radical, and then by polymerization.

Clark[11] is investigating the reversible oxidation-reduction systems of organic compounds and has summarized the entire field in a very readable form. He is building a series of "oxidation-reduction indicators suitable for the measurement of oxidation-reduction 'intensity.' These are comparable to the acid-base indicators used for the measurement of acid-base 'intensity.' "

The investigations of both Conant and Clark have as their ultimate goal the discovery of the mechanism of biological processes. The biological implications of electrode potentials are just now being discovered, most probably for the reason that "the attractiveness of preparing organic compounds by electrolytic processes inevitably diverted attention from equilibrium states to a variety of dynamical problems of seemingly more direct practical importance."[11]

Complete data are now at hand for twenty-six different phenol indophenols, which represent different degrees of desirability as oxidation-reduction indicators. In the use of these indicators the pH must be specified and fairly rigidly maintained if relative oxi-

[9] Conant and Pratt, *J. Am. Chem. Soc.*, 48, 3178 (1926).
[10] Conant and Pratt, *J. Am. Chem. Soc.*, 48, 3220 (1926).
[11] Clark, *Chem. Rev.*, 2, 127 (1925).

dation-reduction intensities, when measured, are to have any significance. These indophenols show two kinds of color change. One is the ordinary acid-base indicator change—a rather pale reddish color in acid and an intense blue in alkaline ranges. The other is the oxidation-reduction change from the color of the oxidant (red or blue) to that of the reductant (practically colorless). Electrometrically this latter change can be measured from 0 to 100% transformation, but visually only within a small range. In solutions around 0.001 molar it is possible to pick out color distinctions in the zone between 70 and 95% reduction (decolorization). Therefore more compounds will be required to cover a given range of reduction potential than would be necessary if the visual perception of decolorization were more effective. A selection has been suggested for the compounds most likely to prove useful in measurement of oxidation-reduction potentials between approximately + 0.07 and + 0.27 volt at pH 7.0.[12]

The paper [13] on "methylene blue" gives a complete review of the uses of this compound in biological and allied work, and includes an excellent bibliography of the whole field. The substance cannot readily be used as a practical reduction indicator for precise measurements.

A potentiometric and spectrophotometric study of meroquinones of the *p*-phenylenediamine and benzidine series [14] is an extension of the study of the simple quinone-quinol system to the more complicated compounds of the diamine-diimine system. The compounds investigated are *o*-tolidine, benzidine, benzidinetrisulfonate, dichloro-*o*-tolidine, Wurster's red, *p*-phenylenediamine, and Wurster's blue. The complexity and the instability of the systems render them of little practical importance for the precise studies of biological oxidation-reduction.

The indicators and potentiometric methods which have been developed by Clark have now been applied to a study of the oxidation-reduction systems such as cell suspensions, washed tissues, glutathione, and growing cultures of bacteria.[15] "It is not at all clear what relation the potentials of a cell suspension bear to conditions within the living intact cell. This is, after all, one of the fundamental problems."

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[12] Gibbs, Cohen and Cannan, *U. S. Public Health Reports*, 40, 649 (1925).

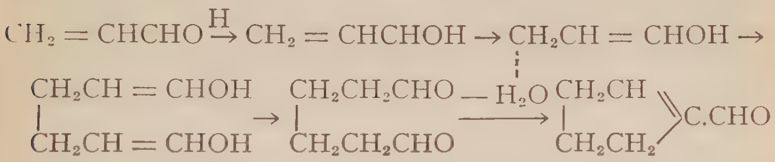
[13] Clark, Cohen and Gibbs, *U. S. Public Health Reports*, 40, 1131 (1925).

[14] Clark, Cohen and Gibbs, *U. S. Public Health Reports*, 1926. Supplement No. 54.

[15] Cannan, Cohen and Clark, *U. S. Public Health Reports*, 1926. Supplement No. 55.

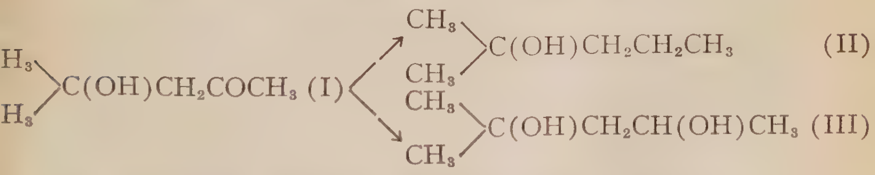
There is entirely too much of valuable information in these papers to permit even abstracting in such a limited space, for an entire field is discussed at length in them. It is hoped that the field will be reserved for future investigation by Clark and his collaborators.

Reactions at the Cathode. In continuing the study of the electrolytic reduction of α, β-unsaturated aliphatic aldehydes begun by Read and Hibbert,[16] acrolein[17] has been reduced in dilute H_2SO_4 on a lead cathode. The products formed are propionaldehyde, allyl and propyl alcohols, Δ′-cyclopentene aldehyde and probably traces of Δ′-cyclopentene carbinol. In accordance with previous work the mechanism suggested is:



Nitrourea in 20% H_2SO_4 is reduced on a mercury cathode in a divided cell cooled to 5-10° C. by a current density of 0.06 ampere per sq. cm. to semicarbazide sulfate. The product may be crystallized in about 61-69% yields by evaporating the solution at temperatures below 55° C.[18]

On lead cathodes in 10% H_2SO_4 with a current density of about 1 ampere per sq. dm. diacetone alcohol (I) is reduced to dimethylpropyl carbinol (II) and 2-methyl-2, 4-pentanediol (III).



These compounds represent the reduction of the carbonyl group (CO) to the hydrocarbon (CH_2) and alcohol (CHOH) groups respectively. The cathodic surface must be especially prepared by repeated oxidation and reduction in dilute H_2SO_4.[19]

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[16] *J. Am. Chem. Soc.*, **46**, 983 (1924).

[17] Read and Freer, *J. Am. Chem. Soc.*, **48**, 1401 (1926).

[18] Ingersoll, Bircher and Brubacker, *Organic Syntheses*, 5, 93. New York, Wiley (1925).

[19] Read and Fletcher, *Trans. Am. Electrochem. Soc.*, 47, 93 (1925).

Lowy has studied the reduction of indigo[20] in an especially built apparatus from which air was excluded. The results show that in solutions of NaOH on a cathode of mercury the current efficiency (a) decreases with an increase in current density, (b) increases with increasing temperature and (c) increases with increasing concentration of alkali. The maximum current efficiency was 94%.

The technical importance of *p*-phenylenediamine and aminosalicylic acid led to the study of their preparation by Norris and Cummings.[21] *p*-Phenylenediamine was prepared in 91.5% material and 85% current yields by reducing *p*-nitroaniline in 17% HCl on a carbon cathode with a current density of 11.2 amperes per sq. dm. at a temperature of about 73° C. The current and material yields were raised slightly by the addition of $TiCl_4$ as a carrier. In the presence of $TiCl_4$ it was possible to reduce benzeneazosalicylic acid in better than 90% yields to aminosalicylic acid which could be separated as the hydrochloride. Over 90% of the $TiCl_4$ was recovered. Fumaric acid is reduced in dilute H_2SO_4 without a diaphragm on a perforated lead cathode with a current density of 6.5 amperes per sq. dm. in 85% yields to succinic acid. Maleic acid is reduced to the same compound in 82% yields but requires the use of a diaphragm. Cinnamic acid has also been reduced to hydrocinnamic acid in good yields.

For pedagogical purposes and for the small scale reduction of organic compounds a short-circuited cell has been found very convenient. A zinc amalgam in H_2SO_4 serves as the anode and is connected directly to a platinum or silver cathode in H_2SO_4 contained in a porous pot. A reducing power is built up on the cathode and can be used for reduction reactions.[22]

Reactions at the Anode. The electrolytic oxidation of *o*-nitrotoluene in 20% nitric acid solution gives only at best about 4% yields of *o*-nitrobenzoic acid; there is, however, the formation of much resinous material with oxalic acid and an evolution of CO_2. A divided cell is required. On the other hand, a divided cell is not required for the oxidation of *p*-bromotoluene in nitric acid solution. Over 100% yields are obtained, based on the amount of current used, because there is some purely chemical oxidation of the toluene derivative to *p*-bromobenzoic acid. In both of these instances strong stirring is required because no solvent is used.[23] Another instance of the use of nitric acid as the electrolyte for oxidations is in the oxidation of toluene to benzaldehyde in a divided cell.[24] Platinum electrodes were most desirable; graphite plates disintegrated too readily to produce good results. Acetone, alcohol, and carbon tetrachloride were unsuitable as solvents; therefore stirring was necessary to keep the mixture in a good state of emulsion.

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[20] Nevyas and Lowy, *Trans. Am. Electrochem. Soc.*, **50**, preprint (1926).
[21] *Ind. Eng. Chem.*, **17**, 305 (1925).
[22] Brockman, *Trans. Am. Electrochem. Soc.*, **51**, preprint (1927).

The mechanism of the electrochemical chlorination of benzene has been somewhat clarified by Croco and Lowy,[25] who have shown that, while the formation of chlorobenzene is not necessarily electrochemical in nature, the formation of the higher chloro compounds is dependent upon the passage of the current. The agitation of benzene with strong hydrochloric acid in the same quantities and under similar conditions as when the current is passed forms chlorobenzene just as if the current were used. The same is true with the formation of bromobenzene without the current. But in the HBr electrolyte no higher bromination compounds of benzene are formed even when the current is passed. The rate of bromination but not the rate of chlorination is changed by the addition of iron as a carrier. The relations of time, temperature, current density, to the rate of reaction were studied.

The electrodeposition of rubber on the anode has been mentioned in the previous volume of this series.[26]

The electrolysis of benzylmagnesium chloride in an especially constructed air-tight and moisture-proof apparatus between platinum electrodes gave 50% current yields of dibenzyl, 100% yields of magnesium, and some magnesium chloride.[27] Phenyl magnesium bromide gave less satisfactory results due to side reactions of an uncertain nature. Metallic magnesium is deposited in both instances on the cathode, the magnesium bromide or chloride is formed at the anode, and it is presumed that the hydrocarbon is formed at the anode.

RESEARCH SUGGESTIONS

From the standpoint of research problems, the field of electro-organic chemistry is wide-open. Even a casual perusal of the literature will indicate the almost innumerable contradictions. Much of the previous worl must be repeated in order to clarify the situation. A few of the more simple and more pressing points may be mentioned.

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[23] Conn and Lowy, *Trans. Am. Electrochem. Soc.*, 50, preprint (1926).
[24] Mann and Paulson, *Trans. Am. Electrochem. Soc.*, 47, 101 (1925).
[25] Croco and Lowy, *Trans. Am. Electrochem. Soc.*, 50, preprint (1926).
[26] Survey of American Chemistry, 1, 172 (1927).
[27] Gaddum and French, *J. Am. Chem. Soc.*, 49, 1295 (1927).

1. There are five theories to explain what happens when a solution of the sodium salt of an aliphatic acid is electrolyzed. More quantitative data are needed to settle the question.
2. The preparation of organic compounds which are of interest industrially or relatively unavailable is of immediate value. Only iodoform, *p*-aminophenol, piperidine, and anthraquinone are prepared commercially at present.
3. The oxidation of hydrocarbons to aldehydes and acids.
4. The halogenation of hydrocarbons.
5. The electrolytic sulfonation and nitration by the use of dilute solutions of the respective acids.
6. The utilization of both anode and cathode compartments of the electrolytic cell for simultaneous oxidation and reduction reactions.
7. The use of the alternating current for electrolysis.
8. The use of catalysts and carriers in electrolytic oxidations and reductions.

Chapter XI.

Heavy Acids.

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George Lunge in his introduction to "The Manufacture of Sulphuric Acid and Alkali" (1903) said:

"It can be truly said that the manufacture of acids and alkali is the foundation upon which the whole chemical industry of our times is built up, and that such industry cannot be much developed in any country not possessing a flourishing alkali trade, or not being at least specially well situated for buying the produce of the latter."

The disappearance of the Leblanc process weakened the linkage between acids and alkali, and the application of synthetic processes to the production of nitric and hydrochloric acids has effectually severed the long existing bond, so that today the manufacture of mineral acids is no longer necessarily associated with the production of alkali.

The changed conditions have brought along a need for economic research as an adjunct to fundamental and applied research, and the year 1926 has been noteworthy for the recognition and important position accorded to the group of studies generally classed as economic research.

Synthetic ammonia, for example, is affecting the tonnage of salt cake produced from salt and niter cake because ammonia oxidation tends to supplant Chilean nitrate as the source of nitric acid. New processes of caliche extraction in Chile may reduce the cost of sodium nitrate, but the balance sheet is again being altered by the growing output of hydrochloric acid synthesized from chlorine and hydrogen, and available at low prices because sales of such acid enable the manufacturer of electrolytic caustic soda to get rid of surplus chlorine.

Sulfuric Acid. The year 1926 brought pyrites back again as one of the important raw materials for sulfuric acid manufacture, thus completing an interesting cycle in the history of sulfur and pyrites. In 1896 about 70% of the sulfuric acid made in the U. S. A. was "brimstone" acid from sulfur. In 1906 about 12% was produced from sulfur, and just prior to the Great War sulfur had practically disappeared in favor of pyrites. The War period brought sulfur back again and by 1922 about 70% of the production originated from sulfur. While 1926 data are not yet available, it has been evident from pyrites importation figures that sulfur, because of its price, has lost ground and probably did not furnish more than 60-65% of the total sulfuric acid production.

In other countries, notably Germany, sulfuric acid is being made on a commercial scale from calcium sulfate, and foreign patent literature gives evidence of considerable research activity in this field. Neumann [1] has reviewed in detail the issued patents on the recovery of sulfuric acid from gypsum, and a description of the Bayer plant at Leverkusen has also appeared.[2] The Rhenania process is disclosed in a British Patent specification,[3] while Marchall [4] has discussed the Rhenania reaction.

Marx [5] has patented the distillation of sulfur from sulfide ores under a high vacuum, and some experimental work is being carried out on the splitting off of SO_3 from iron and aluminum sulfates under high vacuum conditions.

The Grasselli Chemical Company [6] describes a means for securing SO_2 for sulfuric acid manufacture by using sulfur as a fuel in an internal combustion engine, while Robinson [7] has also patented a similar use with or without the addition of hydrocarbon fuels.

The concentration of SO_2 from dilute burner gases and metallurgical operations by an absorption process is described by Howard.[8] The dry burner gases are scrubbed with a liquid cyclic hydrocarbon free from water. The hydrocarbon, when heated, liberates the SO_2 and can be reused.

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[1] *Z. angew. Chem.*, 39, 1537 (1926).
[2] *Z. angew. Chem.*, 39, 169 (1926).
[3] Brit. Pat. 244,078 (Dec. 2, 1924).
[4] *Bull. soc. chim.*, 39, 401 (1926).
[5] U. S. P. 1,574,987 (March 2, 1926).
[6] Brit. Pat. 240,801 (Oct. 4, 1924).
[7] Brit. Pat. 238,621 (May 23, 1924).
[8] U. S. P. 1,606,299 (Nov. 9, 1926).

The relative productions of sulfuric acid by the chamber and contact systems in 1926 show a gain by the contact method as compared to preceding years. Two plants, formerly using the chamber system exclusively, have added contact units and at other chamber plants, consideration is being given to contact acid production.

The fertilizer industry operated through 1926 on a low tonnage cutput thus decreasing the demand for chamber acid, and the purchase by an important corporation of the U. S. Liljenroth patents for phosphoric acid manufacture by the electric furnace method, may mean a further decrease in chamber sulfuric acid consumption. It seems obvious that freight charges on the inert constituents of ordinary 16% acid phosphate will tend towards its replacement as a fertilizer ingredient by more concentrated products such as ammonium phosphate made from synthetic ammonia and electric furnace phosphoric acid.

Hoffmann[9] discusses the development of sulfuric acid manufacture in its relation to the fertilizer industry, and the use of synthetic ammonia and ammonia oxidation products in fertilizers is the subject of a paper by Curtis.[10]

The patent literature of 1926 discloses few suggested improvements on sulfuric acid plant practice. Krafft[11] describes an auxiliary scrubbing tower connected to a lead chamber for removal of acid mist, and the return of the gases to the chamber. The intermediate towers and columns of earlier days would seem to have been designed for the same purpose, and but few of these have remained in use.

The circulation of diluted acid from the chamber bottom, through the gases in the chamber, by means of a pump and spray nozzles has again been the subject of experiment, but results have not yet been reported in the literature.

The use of oxides of nitrogen, obtained from the catalytic oxidation of ammonia, in chamber plants continues to make progress, some ten units being in operation early in 1927. Claims made as to expected improvement of chamber regulation seem to have been borne out in practice.

Lewis and Ries[12] contribute a further discussion to the influence of reaction rate on operating conditions in sulfuric acid manufacture. Shapleigh[13] has described a horizontal SO_3 absorber in which the gases are sprayed with H_2SO_4 cross current to the gas flow.

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[9] *Am. Fertilizer,* **64**, no. 13, 75 (1926).
[10] *Am. Fertilizer,* **64**, no. 13, 67 (1926).
[11] U. S. P. 1,611,534 (Dec. 21, 1926).
[12] *Ind. Eng. Chem.,* **18**, 213 (1926).

Monsanto Chemical Works[14] in a British specification claim as a catalyst for SO_3 production, an artificial zeolite containing pentavalent vanadium in non-exchangeable form, and state 430-450° C. as a desirable operating temperature.

Hydrochloric Acid. The past year was notable for the decline in production of hydrochloric acid made from salt and sulfuric acid. It has been estimated that, on the basis of the available salt cake furnaces in the U. S. A., the total output for the year was not over 20% of capacity. By-product hydrochloric acid from electrolytic caustic soda and from the chlorination of hydrocarbons was partly responsible, but the gradual disappearance of hand blown window glass in favor of machine drawn sheet glass also played its part. The hand plants used salt cake as the main source of Na_2O in the glass batch, whereas the machine plants use principally Na_2CO_3.

Some sodium sulfate is also coming on the market from Western and Canadian dry lakes, but so far this material has had little effect on the Eastern consuming market which is also the seat of major production of salt cake and hydrochloric acid.

The decline in the demand for salt cake and the low price of hydrochloric acid have resulted in the continued use of mechanical furnaces and the shutting down of hand operated muffle units. The Bezanson and Maxim mechanical furnace[15] referred to in the previous issue of this book[16] is being used as a source of hydrochloric acid gas for an organic reaction in one plant and satisfactory results are reported.

The use of rubber lined vessels for hydrochloric acid storage, transportation, and for reactions carried on with hydrochloric acid at temperatures not exceeding 80° C., continues to increase. A number of patents relating to methods of securing lining adherence[17, 18, 19, 20] have been issued. One manufacturer of rubber lined equipment claims to have developed a special composition which permits the use of temperatures up to 92° C.

[13] U. S. P. 1,608.006 (Nov. 23, 1926).
[14] Brit. Pat. 266,007 (Feb. 15, 1926).
[15] U. S. P. 1,544,798 (July 7, 1925).
[16] A Survey of American Chemistry, 1, 70 (1926).
[17] Griffiths, U. S. P. 1,575,681 (March 9, 1926).
[18] Griffiths, U. S. P. 1,591,373 (July 6, 1926).
[19] Radabaugh, U. S. P. 1,574,690 (Feb. 23, 1926).
[20] Warner, U. S. P. 1,584,413 (May 11, 1926).

The use of a sulfur-coke concrete for hydrochloric acid storage vats has been suggested by Kobbe.[21]

It seems surprising, in view of the fact that anhydrous hydrochloric acid gas is compressible to a liquid under 40 atmospheres at 10° C.,[22] and further the liquid does not attack metals, except aluminum,[23] that no attempts have apparently been made to develop shipping containers for the anhydrous liquid acid.

Nitric Acid. The principal feature in nitric acid production has been the commercial operation of ammonia oxidation units. The decreased price of ammonia through improvements in synthetic processes and also severe competition has brought the present cost of nitric acid from ammonia slightly below the cost of nitric acid from nitrates. As a result ammonia is today the principal source of nitric acid in Europe and it has made some headway in this country, although Chilean nitrate nitric acid still constitutes the major production.

The early ammonia oxidation units gave considerable trouble from the standpoint of corrosion of constructional materials. Improvements in chrome steel alloys appear to have eliminated much of the difficulty, and the durability of this chrome alloy equipment is now being studied with a great deal of interest.

The producers of Chilean nitrate of soda are devoting their energies to improving the yield of nitrate from the caliche. The so-called Guggenheim process is said to have met with complete success, and in a recent announcement it was stated that the plant originally built for a capacity of 125,000 tons would promptly be enlarged to 500,000 tons per year. Predictions which have been made as to the extinction of nitrates for nitric acid production seem premature because there are still some unknown factors.

The patent literature on ammonia synthesis continues to grow, whereas very little has issued on ammonia oxidation. Krase[24] has detailed some studies made on the removal of NO_2 from ammonia oxidation gases by silica gel. Thompson,[25] in an article on materials, discusses construction materials for ammonia oxidation processes.

As a means for concentrating dilute nitric acid Büsching[26] proposes to introduce a mixture of HNO_3 and H_2SO_4 into the top of a column which is connected at its bottom with a boiler for H_2SO_4.

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[21] U. S. P. 1,612,869 (Jan. 4, 1927).
[22] Faraday, *Phil. Trans.*, 160 (1828).
[23] Gore, *Proc. Roy. Soc.*, 14, 204 (1865).
[24] *Chem. Met. Eng.*, 33, 674 (1926).
[25] *Trans. Am. Electrochem. Soc.*, 50, Preprint (1926).
[26] U. S. P. 1,590,494 (June 29, 1926).

Cuno[27] has published a study of the influence of oxygen on yields from nitrate of soda retorts, and claims the admission of either oxygen or air prevents decomposition.

Nitric, of the three mineral acids discussed in this chapter, demands at present the greater cost study and the more complete collection of data, because it seems to have the greater probability of change.

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[27] *Ind. Eng. Chem.*, **18**, 1298 (1926).

Chapter XII.

Inorganic Salts.

James R. Withrow,

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I. RECENT ADVANCES IN THE STUDY OF SALTS AND NON-METALLIC INORGANIC SUBSTANCES.

Aluminium. Munro and Johnson have previously shown that alumina takes up a greater amount of water than of any other vapor. They now show [1] the sorption of water vapor by alumina gel at various temperatures and pressures. Both Freundlich's and Patrick's equations apply to the isotherms for 60 and 80°, while neither equation applies to the isotherms obtained when the partial pressures approach the vapor pressure of the liquid at the temperature of the sorbent. Trouton's sorption rule holds approximately over the temperature range studied, *i.e.*, 35.5 to 80°.

Ammonia.* Burk [2] has studied the thermal decomposition of ammonia upon the surface of a molybdenum wire and says that the decomposition was apparently of zero order. The reaction was unretarded by hydrogen but was retarded by nitrogen. The observed heat of activation for the decomposition was found to be 53,200 calories, which was shown to be the true heat of activation. Yost,[3] working on catalytic effect of silver ammonia ion in the oxidation of ammonia by peroxysulfates, finds that the rates of oxidation of NH_3 by $S_2O_8^{--}$ were proportional to the concentration of $S_2O_8^{--}$ and $Ag(NH_3)_2^+$, but were affected only slightly by the concentration of NH_3 and OH^-. The increase caused by NH_3 may be due to the formation of small amounts of $Ag(NH_3)_3^+$, which is more active; and OH^- may decrease the rate by forming un-ionized $Ag(NH_3)_2^+ OH$. Gibson and Phipps [4] worked on conductance of solutions of alkali metals in liquid ammonia and in methylamine and found that the conductances of solutions of Na and K in NH_3 and of Cs, CsI and K in methylamine are at temperatures below —33° in agreement with those of Krause in NH_3. The temperature coefficient of conductance, dlog *R*/ *dt,* is independent of temperature, that is, the conductance is an exponential function of temperature at all dilutions. The metals are less ionized in methylamine than in NH_3. The minimum in the molecular conductance occurs at a lower concentration in NH_3 than in methylamine. The results are in accord with the view that the negative carriers are electrons largely combined with solvent mols, the degree of solvation diminishing as the temperature rises. Bergstrom[5] studied the action of the electronegative elements selenium, tellurium, arsenic and also a solution of sulfur in liquid ammonia upon cyanides and confirmed the reaction equilibrium for sulfur dissolved in liquid NH_3, as $10S + 4NH_3 \leftrightarrows 6H_2S + N_4S_4$, a reaction proposed by Ruff and Geisel from their study of the action of metallic cyanide solutions upon a solution of sulfur in liquid NH_3. Bergstrom found that several other reactions and equilibria exist besides the above when sulfur dissolves in liquid NH_3. Selenium has an extremely slight solubility and both sulfur and selenium behave as weak nitridizing (de-electronizing) agents in liquid NH_3. Solutions of cyanides in liquid NH_3 react readily with sulfur and selenium, slowly with tellurium and not at all with arsenic. Kraus and Whyte[6] have endeavored to determine the nature of the oxidation products obtained with Na and K in liquid NH_3, by a controlled stream of O_2 passed through a solution of the metal in liquid NH_3 in a weighed tube at liquid NH_3 temperatures. The volume of O_2 absorbed was measured and the weights of the products of the reaction were determined by weighing the tube at the end of the reaction. Slow oxidation of K first gave KOH and KNH_2; further oxidation of the latter yields KNO_2 and KOH. On rapid oxidation K_2O_2 forms; this yields K_2O_4 later. There was no evidence that K_2O_3 was produced. Na behaves like K upon slow oxidation in liquid NH_3, and yields Na_2O_2 on rapid oxidation. No evidence was found indicating the formation of Na_2O_3. K_2O_4 dissociates at temperatures above 300°. The reaction is reversible but the pressures depend upon the O_2 content of the solid phase. The final product of dissociation corresponds to the formula K_2O_3. K_2O_4, exposed to the action of moisture, loses O_2 irreversibly between 100 and 200°. Bergstrom[7] also studied reactions of the type $Cl_2 + 2KOH = KCl + KClO + H_2O$. He finds KNH_2 reacts with lead and all elements more electronegative than lead, provided the alkali metal salts containing these elements in mono-atomic anions are soluble in liquid NH_3. These reactions are all of the type named. The reactions between aqueous solutions of bases and Sn, As or P are also of this type. The H_2, AsH_3, and PH_3 obtained in these cases results from hydrolysis of the potassium stannide, arsenide, or phosphide, respectively produced. K and Na ammonostannites [$KSn(NH_2)_3$, etc.] were prepared. They are white solids, very reactive with water and derivatives of bivalent Sn. Groening with Cady,[8] investigating the decomposition potentials and metal overvoltages in liquid ammonia and in water, find that the dynamic decomposition voltages of nitrates and chlorides are lower in ammonia than in water. The iodides and the nitrites are exceptions. A trace of water in liquid ammonia and a trace of ammonia in water have great effects on the decomposition voltages and overvoltages of copper nitrate. Ammonium salts have the same general dynamic decomposition voltage of about 2.1 volts in dry liquid ammonia. Ammonium bromide and ammonium nitrate show several breaks in the current-voltage curve, evidently caused by different products being formed on the electrodes. Temperature has a very slight effect on the dynamic decomposition voltage in liquid ammonia. Kiehl and Hill[9] have prepared a new salt, ammonium monometaphosphate, and some of its properties were determined and compared with those of sodium monometaphosphate. The monomolecular metaphosphates may enter into reactions of double decomposition when dissolved in water without undergoing polymerization. Bowen,[10] studying properties of ammonium nitrate and its meta-stable inversion, finds, besides the well-known transformation of crystalline ammonium nitrate, that a reversible transformation takes place at approximately 50°C., corresponding with the change, orthorhombic $\leftrightarrows$ tetragonal. At this temperature both forms are metastable. Nevertheless the transformation is, in many respects, more prompt and dependable than most of the stable inversions. Studying the system ammonium nitrate-ammonium chloride, Bowen[11] says that a re-examination of this system gives results that agree with those of Perman as to the position of the liquidus curves and the eutectic, but reveals a series of solid solutions not found by him. It is found that all mixtures from pure ammonium nitrate as far as 8% ammonium chloride crystallize to a homogeneous mix-crystal phase of isometric symmetry. In consequence of the existence of this mix-crystal or solid solution series the phenomenon of the eutectic does not enter until after the limits of solid solution are passed, each member of the series beginning to melt at a successively higher temperature, as pure NH_4NO_3 is approached. The isometric → tetragonal inversion changes from 125.5° for pure NH_4NO_3 to 109° for the solid solution containing 3.5% NH_4Cl. At 109°, the curve of unmixing of solid solutions is encountered and along the curve the phenomena of mixing and unmixing of solid solutions take place and can be directly observed. Thus even changes involving diffusion in the solid state take place with comparative readiness in these materials. In studying the system ammonium nitrate-ammonium sulfate, Bowen[12] says that the method of direct observation of phase changes under the microscope, proves that the rising liquidus in the system $NH_4NO_3 — (NH_4)_2SO_4$ is caused by solid solution as Perman and Howells conclude, and not by the limiting position of the eutectic, a possible alternative suggested by Freeth.

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[1] *J. Phys. Chem.*, **30**, 172 (1926).

* See also Chapters VI and XXXV.

[2] *Proc. Nat. Acad. Sci.*, **13**, 67 (1927).

[3] *J. Am. Chem. Soc.*, **48**, 374 (1926).

[4] *J. Am. Chem. Soc.*, **48**, 312 (1926).

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[5] *J. Am. Chem. Soc.*, **48**, 2319 (1926).
[6] *J. Am. Chem. Soc.*, **48**, 1781 (1926).

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[7] *J. Phys. Chem.*, 30, 12 (1926).
[8] *J. Phys. Chem.*, 30, 1597 (1926).
[9] *J. Am. Chem. Soc.*, 49, 123 (1927).
[10] *J. Phys. Chem.*, 30, 721 (1926).

Arsenic. Rushton and Daniels[13] state that, although octahedral As_2O_3 (m. 275°) is metastable above 100°, the rate of change to the stable monoclinic form (m. 315°) is so slow as to permit measurements of the vapor pressure of the former up to 250° or higher, depending on the rate of heating.

Copper. Bell and Murphy[14] produced basic copper sulfate at 100°C. from CuO and 11.4% $CuSO_4$ solution; at least 6 hours were required for equilibrium to be established. Analysis of the residues after removal of as much mother liquor as possible indicated the formula to be $4CuO.SO_3.4H_2O$.

Cyanides. Guernsey and Sherman[15] found the best cyanide on the market to contain at least 2 or 3% of non-cyanide alkali. They developed a method for study of the thermal dissociation of sodium cyanide. Results are shown for the dissociation in an atmosphere of helium at 600, 1000 and 1050° and in an atmosphere of nitrogen at 1050, 1100, 1200, 1220 and 1255°. Sodium carbide results from the dissociation as well as sodium, carbon and nitrogen. The vapor above sodium cyanide consists largely of decomposition products. Thus at 1050° the partial pressures in millimeters of mercury in a helium atmosphere are approximately as follows: Na, 117; sodium carbide, 21.0; N_2, 108; sodium cyanide, 21.0. At all temperatures employed sodium carbides largely dissociated to Na and C.

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[11] *J. Phys. Chem.*, **30**, 726 (1926).
[12] *J. Phys. Chem.*, **30**, 736 (1926).
[13] *J. Am. Chem. Soc.*, **48**, 384 (1926).
[14] *J. Am. Chem. Soc.*, **48**, 1500 (1926).
[15] *J. Am. Chem. Soc.*, **48**, 695 (1926).

Hydrogen. Phipps and Taylor[16] call attention to the magnetic moment of atomic hydrogen prepared by the method of Wood. When studied without the magnetic field, a sharply defined slate-blue line on a white (or slightly yellowish) background resulted after an exposure of an hour or less to the discharge. With the magnetic field on, the central part of the line showed a distinct separation into two branches. Preliminary calculations point to a probable value of one Bohr magneton as the magnetic moment of the hydrogen atom. Browne and Wilcoxon[17] study the formation of sodium trinitride by ammonolysis of sodium nitrate with sodium amide. They say hydronitric acid may be regarded not only as ammononitric acid, but also as hydrazonitrous or as ammonohydrazonitrous acid. $NaNO_3$ undergoes ammonolysis in contact with fused $NaNH_2$, with the formation of NaN_3 at 175°. A yield as high as 65.7% has been obtained on the basis of the equation: $NaNO_3 + 3NaNH_2 = NaNH_2 + 3NaOH + NH_3$.

Potassium. Hill and Miller[18] investigated ternary systems consisting of $K_2CO_3 + Na_2CO_3 + H_2O$ at temperatures from 20 to 50°, and solubility determinations have been made and the phases studied at six intermediate temperatures. The formula of the hydrated K_2CO_3 stable at room temperature is $K_2CO_3 . 3/2\ H_2O$. There is no monohydrate at any temperature. At temperatures below —6.2° the stable hydrate has the formula $K_2CO_3 . 6H_2O$. Burrows and Brown[19] have studied the decomposition of potassium chlorate with reference to spontaneous decomposition temperatures using manganese dioxide, ferric oxide and mixtures of these as catalysts, finding that spontaneous decomposition takes place at definite temperatures for each mixture. The minimum temperature is 292°, the proportions for that temperature being

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[16] *Science*, **64**, 480 (1926).
[17] *J. Am. Chem. Soc.*, **48**, 682 (1926).
[18] *J. Am. Chem. Soc.*, **49**, 669 (1927).
[19] *J. Am. Chem. Soc.*, **48**, 1790 (1926).

$2KClO_3$ to MnO_2. All mixtures containing between 10 and 60 mols. of Fe_2O_3 per 100 mols. of mixture decompose spontaneously at 324°. When a mixture of equal weights of MnO_2 and Fe_2O_3. is used as a catalyst, the spontaneous decomposition temperature is lower than for an equal weight of Fe_2O_3. Sometimes it is lower, and sometimes higher than for an equal weight of MnO_2. Frazer, Lovelace and Taylor[20] have measured the vapor pressures of potassium nitrate solutions at 19.94°C., from 0.1 to 2.9 N. Kiehl and Wallace[21] describe an apparatus with mercury as the confirming liquid, for measuring by the static method dissociation pressures of compounds giving a condensable vapor. Equilibrium was reached from higher temperatures and pressures where reactions were found to be feasibly reversible. The dissociation pressures of the following closed system have been measured: $xK_2H_2P_2O_7 \overset{\Delta}{\rightleftarrows} 2(KPO_3)_x + xH_2O$; $xNa_2H_2P_2O_7 \overset{\Delta}{\rightleftarrows} 2(NaPO_3)_x + xH_2O$; $xKH_2PO_4 \overset{\Delta}{\rightleftarrows} (KPO_3)_x + xH_2O$; $2NaH_2PO_4 \overset{\Delta}{\rightleftarrows} Na_2H_2P_2O_7 + H_2O$.

Silicon. Parks and Kelley[22] say that it seems reasonable to conclude that the heat capacity of a simple silicate, such as calcium silicate, can be accurately estimated, except at the very lowest temperatures, from the known heat capacities of its component oxides. Quig and Wilkinson[23] find that in the preparation of disilicon hexachloride, the ferric chloride formed by the chlorination of a mixture of iron and silicon does not act as a catalyst to increase the yield of lower chloride of silicon nor to lower the temperature at which silicon is chlorinated. The yield of silicon hexachloride can be increased by passing silicon tetrachloride with chlorine over ferrosilicon heated to 200°. This increase is due to the retarding of the final chlorination of disilicon hexachloride to silicon tetrachloride and not to the reduction of the latter by silicon. Nutting,[24] during a study of the hydration of silica, alumina and ferric oxide, noticed that alumina became more and more colored as its hydration increased. The anhydrous oxide, Al_2O_3, is

[20] *J. Phys. Chem.*, **30**, 1669 (1926).
[21] *J. Am. Chem. Soc.*, **49**, 375 (1927).
[22] *J. Phys. Chem.*, **30**, 1175 (1926).
[23] *J. Am. Chem. Soc.*, **48**, 902 (1926).
[24] *Science*, **65**, 279 (1927).

snow white by either reflected or transmitted light. The hydrated form, $Al(OH)_3$, is a decided tan or even brown by transmitted light, but the complementary bluish white by reflected light. Silica shows a precisely similar effect as the SiO_2 goes over to the orthosilicic acid, $Si(OH)_4$. In other words, these hydrated oxides show a pronounced dichroism while the oxides do not. This dichroism is a useful qualitative test for the degree of hydration.

Sulfur and Selenium. Taylor and Wesley[25] have made measurements of the velocity of combination of hydrogen sulfide and sulfur dioxide in Pyrex reaction tubes at temperatures ranging from 370 to 730°C. The velocity was found to be proportional to the surface area of the reaction chamber, which proves that the glass surface acts as a contact catalyst for the reaction.

The temperature coefficient was found to decrease with a rise in temperature; measurements of the velocity at constant temperature show it to vary directly as the partial pressure of the sulfur dioxide and as the partial pressure of the hydrogen sulfide raised to the 1.5 power. Mason and Mathews[26] studied the effect of ultraviolet light on the oxidation of sodium sulfite by atmosphere oxygen and found that there is no apparent relationship between the light absorption of the catalyst and their action upon the photochemical oxidation of sodium sulfite. Draves and Tarter[27] find that sodium trisulfide was formed when metallic sodium was allowed to react in absence of air with an excess of free sulfur in dilute solution in boiling toluene. The formation of potassium pentasulfide under like conditions was indicated.

It was little dreamed while writing of the indefatigable work of Lenher on selenium last year, that he was even then suffering from the preliminary stages of a fatal affection from too close contact with selenium oxychloride. His loss this spring is an irreparable one to selenium investigation.

Brode[28] has studied the dissociation of potassium iodide and the absorption spectra of iodine and potassium iodide. Absorption spectra of I(0.0003N) in alc., aq. KI + (0.125 g./l.) and CCl_4 are given in curves for the range of frequencies 400 to 1300 f (f = vibrations ÷ seconds × 10^{12}). The satellite band appearing under different conditions in absorption spectra of KI has the same frequency as the first band of I in KI, and can be completely removed by adding a few drops of $Na_2S_2O_3$. It is therefore due to free I in the solution and not to KI. A light filter to remove visible light and transmit most of the ultra violet light to a frequency of 1150 f may be made by dissolving I in pure CCl_4 (must be free from alcohol). Hildebrand and Ruhle [29] have measured the decomposition potential of fused lead chlorides diluted with varying amounts of potassium chloride at various temperatures from 500 to 600°. The relation between the composition and activity coefficient of molten lead chloride has been determined at mole fractions of potassium chloride between 0 and 0.4 for 550 and 600°. The decomposition potential of pure, molten lead chloride corresponds to a free energy value of —58,700 cal. at 498°, which is shown to be in substantial agreement with the value at 25° obtained by Gerke. Nichols and Derbigny [30] find that nitrous oxide is reduced by aqueous solutions of titanous chloride, stannous chloride and sodium sulfite, with the formation of ammonia, hydroxylamine and nitrogen, respectively. Taylor and Denslow [31] studied the thermal decomposition of nitrosyl chloride by a dynamic method, between the temperatures of 700 and 900°C., the rapidity of the reverse reaction being overcome by increasing the rate of flow of the gas by diluting with nitrogen. The effect of an increased surface of reaction has been studied and shown to be negligible within the limits of experimental error. The temperature coefficient and energy of activation appear to have values of 1.025 and 6000 calories respectively. Schumacher [32] gives a new method for determining the melting points of certain oxides. BaO, SrO, and CaO melt at 2196°K., 2703°K. and 2849°K., respectively. Phipps and Brode [33] suggest that the Strassfurt blue in rock salt is an electronic color, and a tentative explanation of the behavior of its absorption curves with heat is given. Lambert [34] has studied the ternary system silver bromide-potassium bromide-water and has determined the equilibrium diagram from the known data for each one of the 3 binary systems involved and from his study of the solubility of AgBr and KBr coexistent in aqueous solution in the presence of both solid salts with change of temperature up to 100°. Windsor [35] prepared the new double fluorides of zirconium by dissolving ZrO_2 in HF, adding an equivalent amount of the base in EtOH and either crystallizing or precipitating with Me_2CO. All were white and transparent when dry and were soluble in EtOH and in hot and cold H_2O. Harkins and Zollman [36] have studied effects of bases, salts and acids upon the interfacial tension between aqueous sodium oleate solutions and benzine.

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[25] *J. Phys. Chem.*, 31, 216 (1927).
[26] *J. Phys. Chem.*, 30, 414 (1926).
[27] *J. Am. Chem. Soc.*, 48, 1527 (1926).
[28] *J. Am. Chem. Soc.*, 48, 1877 (1926).

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[29] *J. Am. Chem. Soc.*, **49**, 722 (1927).
[30] *J. Phys. Chem.*, **30**, 491 (1926).
[31] *J. Phys. Chem.*, **31**, 374 (1927).
[32] *J. Am. Chem. Soc.*, **48**, 396 (1926).
[33] *J. Phys. Chem.*, **30**, 507 (1926).
[34] *J. Phys. Chem.*, **30**, 973 (1926).
[35] *J. Am. Chem. Soc.*, **48**, 310 (1926).

II. New Uses of Compounds.

Fungicides and Insecticides. Holland, Dunbar and Gilligan [37] show that crude basic copper sulfate is an effective fungicide, easily applied, fairly indicative of leaf surface cover and of reasonable suspension, distribution and adhesiveness. It can be applied in the same concentration as Bordeaux mixture. It is prepared by precipitation from copper sulfate solution at 75° with precipitated calcium carbonate. Leach [38] found that basic lead, magnesium and ferric arsenates were non-toxic to the larva of the Japanese beetle or to plants. Acid lead arsenate was most satisfactory for larval toxicity and least toxic for plants. The U. S. War Department [39] has discovered that a cyanide gas (said to be CNCl) made from NaCN and $NaClO_3$ is very effective in the war against moths and rodents. Marcovitch [40] finds fluosilicates to be highly effective as insecticides. Both the Na and Ca compounds are used. The Ca compound is especially effective against the flea beetle, while the Na fluosilicate readily controls roaches. The undiluted fluosilicate in some cases caused injury to plants, but when hydrated lime is added, injury is avoided. In many cases fluosilicates are less repellant to insects than arsenicals and hence have a broad field of usefulness. They are fully as toxic to insects as arsenic compounds, but much less toxic to man. Roark [41] finds that the results of the tests with the insoluble fluorides as insecticides have been very encouraging. Meanwhile it is suggested that the insecticidal action of the less soluble fluorides be utilized rather than that of the fluosilicates as it is believed that not only will more uniform insecticidal action be obtained, but injury to vegetation will be avoided. deOng,[42] studying potassium xanthate as a soil fumigant, finds that K xanthate and Na xanthate change in an acid medium to xanthic acid, which at moderate temperatures decomposes into CS_2 and alcohol. K xanthate, on account of its solubility in KOH, may be distributed in the soil at any convenient depth and at any concentration. This makes possible the treatment of soils at a lower concentration of CS_2 than is possible where the latter is used pure. Fleming and Reedy [43] suggest the use of waste sulfite liquor as an agricultural spray; it is suggested that "blowpit" liquor from paper mills may be used since its composition approximates that of the lime sulfur spray used as a fungicide and insecticide. These workers found that the final mixture produced settled very slowly and on stirring regains its suspension very easily. Small scale tests have been favorable but field tests remain to be tried out.

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[36] *J. Am. Chem. Soc.*, **48**, 69 (1926).
[37] *J. Agr. Research*, **33**, 741 (1926).
[38] *J. Agr. Research*, **33**, 1 (1926).
[39] *News Edition, Ind. Eng. Chem.*, 20, no. 20, 2 (Oct. 20, 1926).
[40] *Ind. Eng. Chem.*, **18**, 572 (1926).
[41] *Science*, **63**, 431 (1926).
[42] *Ind. Eng. Chem.*, **18**, 52 (1926).

Lime. Lime is such an important chemical resource and its problems are so great not only on the side of use, but also on the side of production, that the Industrial Division of the American Chemical Society set apart its meeting at Richmond, Virginia, for probably the most outstanding Symposium on lime and its problems ever presented. Most of the papers presented at this Symposium appeared in the May number of *Industrial and Engineering Chemistry*. The value of lime to mankind is nowhere better shown than in the use of lime in butter making. Overman [44] shows that lime enables us to control fermentation acidity safely in cream, allowing shipping over wide areas and making possible the supply for tremendous urban needs. Warrick [45] points out lime treatment in disposal of pea cannery waste. Bowles [46] says that at the request of the gypsum industries, Berger undertook a series of tests to determine the adaptability of anhydrite as a cement retarder. Very thorough tests were made on 18 samples of cement from various parts of the country. It was found that anhydrite alone is not a good retarder, though it gives good results when mixed with gypsum. Hardy [47] points out the use of barium carbonate in the production of case-hardening mixture for steel making; of late this new use for carbonate is continuously becoming more and more important and absorbs an appreciable tonnage of the imported materials. Willetts [48] claims a high-temperature ce-

[43] *Chem. Met. Eng.*, 34, 159 (1927).
[44] *Ind. Eng. Chem.*, 19, 571 (1927).
[45] *Ind. Eng. Chem.*, *News Ed.*, March 10, 1927, p. 3.
[46] *Mineral Industry*, 34, 369 (1925).
[47] *Mineral Industry*, 34, 95 (1925).
[48] U. S. P. 1,573,888 (Feb. 23, 1926).

ment adapted for sealing annealing leers; this comprises $BaSO_4$ 60, SiO_2 40 and sufficient Na silicate solution of 43° Bé to form a pasty mixture. Smith [49] states that the use of a mixture of two dehydrating agents, each of which supplies properties deficient in the other, is often advantageous; the use of mixtures of anhydrous barium perchlorate and anhydrous magnesium perchlorate is discussed.

The problem of the use of bisulfates as detergents is solved industrially by Fritz,[50] who makes a cleaning powder adapted for use on porcelain from $NaHSO_4$ or other alkali bisulfate mixed with a quantity of a metallic oxide, such as MgO, which is sufficient to react with only a portion of the bisulfate. Kerr, Marsh, Schroeder and Boyer [51] find that sodium nitrite can be successfully substituted for sodium or potassium nitrate in curing of meat. One fourth to one ounce of sodium nitrite is sufficient to fix color in 100 pounds of meat, the quantity depending on the kind of meat and the process of curing. Shortening of the curing period is obtained, giving equal quality and wholesomeness with meats cured with nitrates. The use of sodium nitrite has been formally authorized by the Department of Agriculture, subject to meat inspection regulations. High temperature whitewash for furnace use is discussed by Arthur, Mitchener and Withrow.[52] Kobbe [53] states that the strength of concrete can be considerably increased by impregnating with sulfur. The treatment process consists of immersing the concrete in a bath of sulfur maintained at 130-150° for several hours. Standard tensile briquettes of cement mortar, which ordinarily break at 150 pounds, are increased in strength to over 1000 pounds per square inch by this treatment, and strength under compression is similarly increased. Water absorption is usually reduced to less than 2-3%. Bates [54] states that impregnating drain tile with molten sulfur greatly increased the tensile strength and reduced absorption, but does not in any manner increase their life in alkali soils. Kobbe [53] also says that wood when immersed in molten sulfur at 150°, either in open tanks or closed cylinders under pressure, will absorb 40-76% of its weight, depending upon the kind of wood, and manner of treatment. Solid carbon dioxide is already finding considerable use as a commercial refrigerant. Killeffer[55] suggests further uses as follows: Refrigerant in light-weight packages to be sent by mail or express; freezing quicksands in excavation work; local anesthetic for surgery and dentistry; shipment or storage at extremely low temperatures (—40 or —50°C.). Solid CO_2 possesses various advantages over ice as a refrigerant.

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[49] *Ind. Eng. Chem.*, **19**, 411 (1927).
[50] U. S. P. 1,599,996 (Sept. 14, 1926).
[51] *J. Agr. Research*, **33**, 541 (1926).
[52] *Ind. Eng. Chem.*, **19**, 591 (1927).
[53] *Chem. Met. Eng.*, **33**, 354 (1926).
[54] *Ind. Eng. Chem.*, **18**, 309 (1926).

III. Advances in Industrial Manufacture and Use of Salts and Non-Metallic Inorganic Substances.

Production of nitrogen compounds by synthetic processes now dominates the world situation, production from byproduct sources is second and Chilean nitrate is a poor third. Plans thus far announced for 1927 indicate that water gas hydrogen will probably supply nearly half of the synthetic ammonia, that byproduct hydrogen will give 40 to 45% and that electrolytic hydrogen will be used for only 10% of this output of 21,000 to 25,000 tons which is estimated for this year. The use of natural gas is about to be developed in Louisiana, where it is abundant, for the production of hydrogen for ammonia; methanol will probably be a byproduct. Claude,[56] pursuing the problem of ammonia synthesis, states that a gaseous mixture containing H, N and H_2O vapor is cooled under "hyperpressure," H_2O is separated and the remaining gases and residual H_2O vapor are passed over a catalyst under the same "hyperpressure" which may be about 1000 atm. deJahn[57] also purified gas for ammonia synthesis. A water gas or producer gas or gas mixture containing H, N and CO in which the ratio of N to H + CO is less than the desired predetermined ratio of N to H, is treated with steam in the presence of a catalyst by which CO is oxidized to CO_2 with the production of an equal volume of H, and prior to completion of the catalytic reaction, there is supplied additional nitrogen by admitting regulated quantities of air to the gaseous system. Liljenroth and Larsson[58] state that steam is reacted upon with vaporized P at a temperature of about 500-700° in presence of catalysts to give hydrogen. It is evident that the P goes to H_3PO_4 which can then be neutralized by NH_3 produced from the hydrogen.

Biddulph-Smith[59] studied the neutrality of $(NH_4)_2SO_4$ by electrometric titration and standard titration with methyl orange. Methyl orange gave 0.01 — 0.02% higher acidity on the same $(NH_4)_2SO_4$ salt. Pure $(NH_4)_2SO_4$ in pure H_2O gives a full yellow to methyl orange, but an electrometrically neutral solution of the concentrated salt is orange colored and reacts acid to litmus and lacmoid. The difference was due to pyridine sulfate. A pyridine sulfate solution neutral by the electrometric method gave the maximum pink color with methyl orange.

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[55] *Ind. Eng. Chem.*, **19**, 192 (1927).
[56] U. S. P. 1,609,058 (Nov. 30, 1926).
[57] U. S. P. 1,610,076 (Dec. 7, 1926).
[58] U. S. P. 1,605,960 (Nov. 9, 1926).
[59] *Gas World*, 84, Coking Section 26 (1926).

A forward step in manufacture of arsenic acid, made by Ambruster,[60] eliminates the usual trouble in this process due to foaming; the bulk of the reaction is caused to take place outside of the main batch kettle and within the pump or agitator below and then, by releasing the gas from a fountain discharge above the level of the surface of the batch in the main kettle, the foam is continuously broken and the gas is liberated in the open space above the batch. This new improvement permits a decided speeding up of manufacture and the utilization of off grade arsenic. Van Leeuwen[61] has developed a coated arsenate of lead. $PbHAsO_4$ is suspended in H_2O in which a known amount of Na oleate is dissolved. Pb acetate equivalent to the Na oleate is then added with vigorous stirring. The product consists of Pb oleate in minute globules intimately mixed with $PbHAsO_4$. When dried, a water repelling powder is obtained in which the particles of arsenate are coated with Pb oleate. More than 0.25% of Pb oleate is required for complete coating. Experiments indicate that the coated $PbHAsO_4$ kills a higher per cent of the beetles than the uncoated, that it spreads evenly on foliage and adheres better than the uncoated compound. It is practically unaffected by rains.

Weber[62] calls attention to the possibility of blanc fixe as a by-product of hydrogen peroxide manufacture. The Ba phosphate produced by the reaction of H_3PO_4 on BaO_2 is further treated with H_3PO_4 and the separated solution thus formed is treated with H_2SO_4 or other material supplying SO_4 ions to form blanc fixe. Hall[63] discusses boiler water conditioning with special reference to high operating pressure and corrosion. Concentration in the boiler water of the chemical used in treatment is a function (a) of the operating pressure and (b) of the concentration of sulfate radical in the boiler water. Soluble phosphates were found to give excellent results in preventing adherent scales which are formed by calcium sulfate and calcium and magnesium silicates. Metzger[64] has developed calcium cyanide-powdered hydrocyanic acid, a new product of manufacture. This is made by treating CaC_2 with HCN, C_2H_2 being evolved; the product contains about 55% CN and is useful as a fumigant. It is said to be safer to handle, more stable and possesses a wider margin of safety in application than liquid HCN. Brallier[65] gives brief descriptions of manufacturing processes for preparing chlorides of silicon, titanium, tin, antimony, zinc and aluminum by the treatment of the corresponding metal, or, in the case of silicon and titanium, the metal carbide with chlorine. All the metals named react readily with chlorine at certain temperatures and these reaction temperatures vary from 100°C., for tin and antimony, up to 1000°C. or over, for SiC.

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[60] U. S. P. 1,603,308 (Oct. 19, 1926).
[61] *J. Econ. Entomol.*, 18, 744 (1926).
[62] U. S. P. 1,587,450 (June 1, 1926).
[63] U. S. Bureau of Mines, Reports of Investigations No. 2727.

The old methods of dehydration of organic compounds by the use of lime, dehydrated salts and even metallic sodium as is well known have been practically entirely replaced in recent years in manufacturing, by engineering procedure, particularly where constant boiling mixtures with water are formed. For instance absolute alcohol is practically entirely manufactured on a large scale today by the use of benzol, in the distillation equipment, for sucking the water out of the constant boiling mixture. The same device is used in the manufacture of esters so as to prevent equilibrium being set up early, by the presence of water which can be so readily eliminated by the use of benzol. Salts, lime, and sodium therefore have been displaced by a cheaper and more effective procedure. Traces only of benzol are left in the products. The manufacturing methods have been so perfected that even a trace of benzol cannot readily be detected. Where such trace of benzol is really undesirable (in research for instance) resort must be had in the preparation to the older use of anhydrous salts and lime or sodium. With the object of effecting economies in the quantity of sulfuric acid required in producing available phosphates, Singleton[66] has proposed heating phosphate rock in rotary kiln to a temperature sufficiently high to destroy organic matter, but below the temperature which would decompose the carbonates. The inventor claims that a treatment of this kind effects a saving of eight % in the quantity of sulfuric acid required to convert the phosphate rock into acid phosphate and that the grade of the finished product is increased about 3.5%.

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[64] *Ind. Eng. Chem.*, 18, 161 (1926).
[65] *Trans. Am. Electrochem. Soc.*, 49, 257 (1926).
[66] U. S. P. 1,546,946 (July 21, 1925).

One of the most interesting achievements which have come to the attention of the writer during the year has been the manufacture of smoked salt. The salt used in pickling is smoked before use in pickling meat, thereby securing a greater penetration of smoke ingredients into the meat than in the normal practice of true smoking. It looks as though a revolutionary improvement in meat "smoking" were thus available. The product of this process when properly conducted has a golden brown color with a delicious smoked bacon or ham odor and taste. It can be readily distinguished in many ways and particularly by its odor and taste from numerous substitutes already appearing on the market which consist merely of salt treated with a filtered pyroligneous acid, followed by drying or evaporation. Contrary to superficial expectation the two products are not at all alike even in flavor. The manufacture of true "smoked-salt" as distinguished from the imitation "smoked-salt" has reached a production amounting to many thousands of tons and is a rapidly growing business.

Neville,[67] studying the setting of plaster of Paris, says that the setting occurs in two stages. This is shown by relating rise in temperature to time, and also by measuring the change in volume with time. The two stages are: adsorption accompanied by a contraction in volume and a slight heat effect whereby the two reactants are brought into chemical contact; a resulting exothermic chemical reaction between the adsorbed liquid and the absorbent, with an increase in volume. The relative effectiveness of various substances in accelerating the setting is shown. This effect is not due to increased solubility of $CaSO_4$, but results from the colloidal nature of the mixture of plaster of Paris and water.

Arnold[68] suggests that sodium bicarbonate and nitrogen be made from waste blast-furnace gases. He claims that waste blast-furnace gases are burned in air to convert the CO and H_2 into CO_2 and H_2O with increase in N content of the gases; the gaseous mixture thus formed is compressed and passed into contact with ammoniated brine while under pressure considerably in excess of the hydrostatic pressure of the brine. Cundall[69] described a new process for the recovery of sulfur from gas, based on the catalytic oxidation to free sulfur of the sulfide compounds in the solution leaving the absorber. This process will remove up to 98% of the hydrogen sulfide in the gas and oxidize it to free sulfur of a form extremely valuable in agricultural work due to its extreme fineness. The absorption of the hydrogen sulfide is accomplished by a tower filled with wooden hurdles over which a soda solution is sprayed. Engle[70] describes the gaseous reduction of tungsten and molybdenum oxides in the production of the pure metals. The oxide of tungsten or of molybdenum is placed in a heated tube and a fairly rapid stream of hydrogen gas passed through it. The reduction of WO_3 begins at about 620° C., and that of MoO_3 at about 300° C.; the desired physical structure of the metal powders is obtained mainly by a proper balance of rate of hydrogen flow and temperature rise. Jencke[71] describes the preparation of very pure tungstic acid (H_2WO_4), tungstic oxide (WO_3), ammonium paratungstate ($(NH_4)_{10}W_{12}O_{41}$), and ammonium molybdate.

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[67] *J. Phys. Chem.*, 30, 1037 (1926).
[68] U. S. P. 1,611,401 (Dec. 21, 1926).
[69] *Chem. Met. Eng.*, 34, 143 (1927).

The inside frosting of incandescent lamps has presented a problem to manufacturers for some time. Pipkin[72] describes a satisfactory frosting mixture which has been developed, consisting of 48 to 60% hydrofluoric acid saturated with ammonium fluoride, and enough water and Na_2CO_3 added to bring the acidity down to about 25% hydrofluoric acid. A new cement high in alumina (42% Al_2O_3) is discussed by Bates.[73] It attains maximum strength in 24 hours, and has been satisfactorily used for underwater work, etc. A study of the problem of converting KCl into K_2SO_4 has been undertaken by Fox and Whittaker[74] using the method of the direct treatment of KCl with H_2SO_4. HCl is a byproduct. In the manufacture of nitric acid, Cuno[75] states that an excess of oxygen in the retort prevents in large measure any decomposition of the nitric acid.

IV. RESEARCHES UNDER WAY TO IMPROVE MANUFACTURING PROCESSES AND USES.

Kinney and Guernsey[76] suggest that the occurrence of alkali cyanides in the iron blast furnace affects largely the deterioration of furnace lining. Formation and volatilization of potassium cyanide from hearth is calculated to dissipate only 0.3% of the available heat of the hearth. Though strongly reducing, the cyanides are not thought to be essential to the reduction of iron. It is unlikely that the operation of the furnace would be adversely affected by withdrawal of a small part of gas for recovery of cyanides by condensing the fume. Withdrawal of 10% of the gas at base of stack is estimated to yield 1040 pounds of crude cyanide per day.

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[70] *Trans. Am. Electrochem. Soc.*, **48**, 345 (1925).
[71] *Trans. Am. Electrochem Soc.*, **48**, 299 (1925).
[72] *Ind. Eng. Chem.*, **18**, 774 (1926).
[73] *Ind. Eng. Chem.*, **18** 554 (1926).
[74] *Ind. Eng. Chem.*, **19**, 349 (1927).
[75] *Ind. Eng. Chem.*, **18**, 1298 (1926).
[76] U. S. Bureau of Mines, Technical Paper 390 (1926).

Miller[77] has investigated the effects of ions upon the physical, chemical and colloidal properties of aluminium hydroxides. He finds that in water purification by alum, three chemical factors determine the success: (1) a certain minimum amount of Al ion; (2) an anion of strong coagulation power; (3) properly adjusted H ion concentration of all anions studied. The sulfate yields a "floc" with qualities best suited to water clarification, it being rapid in settling and compact. The pH range over which $Al_2(SO_4)_3$ is effective (5.3-8.6) with a maximum as 5.5, is much broader than that of $AlCl_3$ (7.8-8.6). Cowles[78] states that a sintered product of sodium aluminate is formed from leucite and CaO or other substances containing soda, lime, alumina and silica, in the mol. ratio of $1SiO_2$, 2CaO and substantially less than 1.76 mols. of soda to 1 mol. of Al_2O_3. The sintered product is subjected to leaching. Cowles[79] further specifies heating to a sintering temperature a mixture containing combined alumina and silica, $CaCO_3$ and Na_2CO_3 in such proportions that the furnaced product shall contain 1 mol. of SiO_2 to each 2 mols. of CaO and 1 mol. of Al_2O_3 to each mol. of Na_2O. Na aluminate is dissolved from the resulting mixture by means of H_2O initially containing Na_2O so that the resulting solution shall contain materially less than 1.75 and materially more than 1.10 mols. of Na_2O to each mol. of Al_2O_3.

Eddy[80] has studied some absorbed insecticides. Na_2AsO_3, Na_2AsO_4, K_2AsO_3 and K_2AsO_4 were absorbed on kaolin, diatomaceous earth, fuller's earth, talc and tripoli, the material dried and reduced to a fine dust. The quantity of As absorbed was 0.17-0.42 g. per 100 g. dust, av. 0.24 g. The effectiveness of the carriers as absorbent was: Kaolin $>$ diatomaceous earth $>$ fuller's earth $>$ talc $<$ tripoli. Na_2AsO_4 is probably absorbed in greatest quantity and K_2AsO_4 in least. When large excess of As salt was used the order of removal was kaolin $>$ diatomaceous earth $>$ tripoli $=$ fuller's earth $=$ talc. Talc removed more As than fuller's earth from solutions of Na_2AsO_4 and K_2AsO_4, but the same amount from solutions of Na_2AsO_3 and K_2AsO_3. The variable colloidal nature of the carriers was a disturbing factor. Experiments with these dusts on the Colorado potato beetle (*Leptinotarsa decemlineata*) and the Mexican bean beetle (*Epilachna corrupta*) indicate possibilities for their use against chewing insects without danger to plants. Jenkins and Berger[81] find that As_2O_3 is dissolved in a weak solution of alkali, such as NaOH, and that the alkali metal arsenite thus formed is oxidized to arsenate by air in the presence of Cu or a Cu compound, which serves as a catalyst.

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[77] Colloidal Symposium Monograph, 3, 208 (1925).
[78] U. S. P. 1,591,364 (July 6, 1926).
[79] U. S. P. 1,591,365 (July 6, 1926).
[80] *J. Econ. Entomol.*, 19, 77 (1926).

McDonnell and Hart,[82] studying deterioration of commercially packed chlorinated lime, find that most of the available chlorine lost was converted to chloride, and that there was no marked difference in rate of deterioration between winter and summer manufacture and pack. The average loss for all samples in available chlorine was 1.08% per month for the period covered (15 months); the average for the hottest months was 1.44%, for the coldest, 0.61%; the keeping qualities were not greatly affected by type and size of container, a small difference being noted in favor of metal; the method of pack (hand or machine) showed little difference; an increase in rate of deterioration of some samples was accompanied by a decided increase in moisture; visible light rays seem to have a slight accelerating effect. Dow[83] proposes to mix $CaCl_2$ or other hygroscopic hydrated metallic chlorides with a powder of the chloride in a more nearly dehydrated form, which serves to lessen the tendency to caking. Hall, Robb and Coleman[84] state that direct determinations have been made of the solubility of anhydrite (calcium sulfate) and soluble anhydrite at temperatures characteristic of boiler water. The values for soluble anhydrite agree with those of Boyer-Guillon and Melcher; those for anhydrite agree well with Melcher's values at higher temperatures, but not so well with those at lower temperatures. Whitman and Davis[85] have studied the hydration of lime, particularly the effect of 3 variables—ratio of water to lime, temperature of hydration, and agitation—upon the properties of hydrated lime. The

[81] U. S. P. 1,596,662 (Aug. 17, 1926).
[82] U. S. Dept. Agr., Bull. 1389 (1926).
[83] U. S. P. 1,592,971 (July 20, 1926).
[84] *J. Am. Chem. Soc.*, 48, 927 (1926).
[85] *Ind. Eng. Chem.*, 18, 118 (1926).

quality of the hydrated material was evaluated by three different methods: rate of reaction of the lime suspension with acid; rate of settling in water; and microscopic examination. The best product is prepared by hydrating at moderately high temperatures with excess water. Myers[86] finds that experimental results in large sintering machines indicate excellent possibilities in the production of lime from small stone. Limestone was treated by three different methods on a laboratory scale: (1) limestone mixed with solid fuel and ignited; (2) a low reverberatory arch placed over the pallets or cars; (3) a combination of the two previous methods. The machine is apparently most valuable for fines not exceeding 0.6 cm. in diameter. Coarser materials require longer calcination. Stage crushing and screening will permit the preparation of a series of sizes which can be burned in rotation. A wide choice of fuels is possible, with producer gas and powdered coal apparently the most advantageous. Weber and Nilsson,[87] in a study of the absorption of nearly pure CO_2 by various lime solutions under constant temperature, verify the multiple-film theory of absorption. Dry CaO and $Ca(OH)_2$ absorb a negligible amount of CO_2 under the conditions existing. Haslam and Herman[88] say concerning the effect of time and temperature of burning on the properties of limestone that the optimum temperature for the limes studied was 2000° F. except for Ohio limes and that the plasticity increase is proportional to the decrease in rate of settling.

Abbott, Culver and Morgan[89] have studied the effectiveness against the San Jose scale of the dry substitutes for liquid lime-sulfur. Results obtained in 39 tests with dry calcium-sulfur, 13 with dry sodium-sulfur, and 11 with dry barium-sulfur under practical orchard conditions in 4 states over a period of 3 years showed that the commercial samples of dry Ca-, Na-, and Ba-sulfur, even when used in strengths much greater than that ordinarily employed, do not furnish a satisfactory control of the San Jose scale. The lack of effectiveness of the dry substitutes is thought to be due to their relatively lower content of the higher polysulfides and to the presence of a higher proportion of CaS_2O_3, S and other ingredients of no practical value. Hoover[90] emphasizes methods of recarbonation of lime-soda-softened water. The prevention of after-precipitation is best accomplished by recarbonation with CO_2. The use of other acids is either unsatisfactory or uneconomical. Several methods of generating the gas are available; whatever method is used, it should furnish the gas in a reasonably high concentration and free from impurities which will impart odors or tastes to the waters. Automatic devices for measuring and controlling the gas should be provided. This will greatly expand the use of lime in municipal softening and sanitation.

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[86] Bur. Mines, Reports of Investigations, No. 2762 (1926).
[87] *Ind. Eng. Chem.*, 18, 1070 (1926).
[88] *Rock Products*, 29, 58 (Oct. 30, 1926).
[89] U. S. Dept. Agr., Bull. 1371, 1-26 (1926).
[90] *Ind. Eng. Chem.*, 19, 567 (1927).

Wiberg[91] describes a new method for the production of iron sponge, using carbon monoxide plus a little hydrogen. It is shown that gaseous reduction can be carried out continuously and efficiently, provided the reducing gas is separately generated and then passed over the heated iron ore, and provided a large proportion of the circulating gas is removed from the reduction furnace before it enters the preliminary zone. This by-passed gas is then enriched in CO by coming in contact with incandescent carbon and then enters the final reduction zone. The gas escaping from the reduction furnace will run as high as 72% CO_2. A high quality sponge iron is produced analyzing very low in S and P. Low grade iron ores are suitable. Most of the gangue is removed magnetically after reduction. Henderson and Kracek[92] state that the fractional precipitation of barium-radium chromate affords a means of separating the two elements which is comparable in effectiveness to the best results obtained with the bromide method. The partition factor D is found to be 15.5 for acid solutions. The chromate method may be used to advantage with relatively small quantities of barium-radium mixtures. It may be used for recovering radium in radium-barium solutions which are too lean to be economically concentrated with the chlorine method.

Wilson, Parsons and Chisholm[93] state that $BaMnO_4$ is formed by fusing an alkali metal hydroxide such as NaOH and adding to the fused mass BaO_2MnO_2. The Ba manganate may then be oxidized to permanganate.

A special method is coming into use of graining concentrated fertilizer materials consisting in atomizing the molten material or an extremely concentrated solution of the salt in such a way that the droplets harden in the air resulting in a spherule of the substance. These type crystals are most slowly affected by atmospheric conditions. This method may be applied to calcium nitrate with ammonium nitrate and perhaps some of the ammonium phosphates. In crystallizing U. S. P. magnesium sulfate it has been found that black iron pans are very satisfactory and do not contaminate the salt. Wilson of Rumford Chemical Co. has developed a method of grinding phosphate rock in sulfuric acid which is much cheaper and less troublesome than drying the rock and then graining as was the method formerly used.

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[91] *Trans. Am. Electrochem. Soc.*, 48, 529 (1925).
[92] *J. Am. Chem. Soc.*, 49, 738 (1927).
[93] U. S. P. 1,592,480 (July 13, 1926).

V. RESEARCHES NEEDED TO FURTHER INORGANIC CHEMISTRY AND IN THE MANUFACTURE AND USE OF SALTS AND NON-METALLIC INORGANIC SUBSTANCES.

Fume Problem. The fume problem is always with us. As long as population increases in density, manufactories which produce fumes inevitably will do so also. Particularly unfortunate in relation to the community are those industries whose fumes have a recognizable odor which will carry on the wind for a long distance, such as carbon bisulfide or hydrogen sulfide. The elimination of up to fifty parts per million of hydrogen sulfide from thirty million cubic feet of air per day leaving a plant, is a problem which has found no economic engineering solution.

The dehydration, particularly of organic substances and especially dehydration during and for the assistance of reactions by the use of suitable salts and other non-metallic inorganic compounds, is often expensive, and so troublesome from an engineering point of view and wasteful in yield, that many organic chemical reactions should be carefully studied from the point of view of using more modern ideas which might apply to this type of dehydration, with a view to the elimination of the salts and compounds mentioned.

Gilkey [94] points out that there is need for more research to determine the effect of the concentration of CO_2 upon the rates of calcination of limestone. Blum [95] states electrochemistry needs a knowledge of atomic structure of electrode materials, and the nature of reactions by which electron exchange takes place. It also needs progress in the study of atomic physics. Morey [96] states that the cement industry needs fundamental researches on systems containing the components commonly found in manufacturing, and Bates[73] says that it would be valuable to develop a cement having quick-settling characteristics, but made of readily-accessible materials. In the glass industry, developments may come, Morey[96] suggests, by developing new proportions of the usual glass ingredients. Further investigation of the reduction of low-grade bauxite in the electric furnace is suggested by Krase, Thompson and Yee.[97] Faust[98] suggests as possible future developments in the nitrate industry the elimination of borates, chlorides, and sulfates, and the precipitation of the borates as manganese or zinc borate, the former used in paint technology, and the latter possibly in face powders and fire-retardent paints.

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[94] *Ind. Eng. Chem.*, **18**, 727 (1926).
[95] *Ind. Eng. Chem.*, **18**, 1028 (1926).
[96] *Ind. Eng. Chem.*, **18**, 1023 (1926).

New refractories for glass factory use are an urgent need. A new type of furnace with smaller melting area and larger output is needed. There should be developed a substitute for fuel oil to obtain a clean gas from coal with a B.T.U. value of 450-500 at a cost equal to oil on the basis of 7c per gal. The problem why slips and glazes thin out while standing remains unsolved. The causes of scumming and crazing of glazes has had much attention and requires more. The ceramic industry asks for the use of sillimanite as a glass works refractory, corrosion and erosion phenomena and their bearing on macro structures of refractories and X-ray patterns of mullite and sillimanite, and development of a new refractory that will stand erosion and corrosion of glass batch. What really is glass? The lime industry must study the effect of lime in concrete, the acoustics of lime plaster, fire tests on lime plaster, physical and chemical properties of stuccos. What properties of lime determine the settling rate of carbonated sludge and how can this be accelerated? The action of lime on sugar, strawboard and pickling liquor effluents should be extended.

It is perfectly obvious that not all the published material on salts and inorganic substances could be reviewed in the space available and important material inevitably must be omitted. Many notes of industrial practice have been forced out of the manuscript by space considerations.

[97] *Ind. Eng. Chem.*, **18**, 1287 (1926).
[98] *Ind. Eng. Chem.*, **19**, 276 (1927).

Chapter XIII.

The Common Earths.

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This report will cover those six earthy oxides which form almost exactly 90% of the earth's crust, and so are necessarily of importance to man merely because of their abundance and accessibility, whatever be their specific properties. They are: SiO_2, Al_2O_3, MgO, CaO, Fe_2O_3 and FeO.

General Works. Weiser's book [1] gives an excellent review of the hydrated forms of SiO_2, Al_2O_3 and Fe_2O_3 up to about January, 1926. Sosman's [2] comprehensive book on the properties of pure SiO_2, coming up to about October, 1926, is now being printed. Mellor [3] has already covered SiO_2, MgO and CaO in his thorough fashion, but has not reached Al_2O_3 or the oxides of iron.

Silica. Greig [4] has confirmed Ferguson and Merwin's value of 1710 ± 10° for the melting point of cristobalite, but has made the determination more accurate and now places the point at 1713 ± 5°. The effect of small amounts of impurities in accelerating the transformation of quartz to cristobalite or tridymite is strikingly shown in his experiments.

The structure of high-quartz is now fairly well established, Bragg and Gibbs,[5] in England, having arrived at the same conclusion as Wyckoff.[6] High-cristobalite is also known.[7] The other modifications are not yet known with as much certainty but the English investigators are at work upon them.

The piezo-electric property of quartz has rapidly increased in importance because of its use in the standardization and control of radio frequencies. Experimental work has been done in several physical laboratories, including the Naval Research Laboratory in Washington, Cady's laboratory at Wesleyan University, and Terry's laboratory at the University of Wisconsin.[8]

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[1] Weiser, H. B., The hydrous oxides, New York, McGraw-Hill, 1926.

[2] Sosman, R. B., The properties of silica, New York, Chem. Catalog Co., 1927.

[3] Mellor, J. W., Comprehensive treatise on inorganic and theoretical chemistry, London, Longmans, 1923-1925. Vols. 6, 4, 3, respectively.

[4] *Am. J. Sci.*, (5) 13, 7 (1927).

[5] *Proc. Roy. Soc.* (London), 109A, 405 (1925).

[6] *Am. J. Sci.*, (5) 11, 101 (1926); *Z. Krist.*, 63, 507 (1926).

[7] Wyckoff, *Am. J. Sci.*, (5) 9, 448 (1925).

Holden[9] continued his studies of colored and smoky quartz, finding iron compounds to be the most probable cause of the color of amethyst, while atomic silicon liberated by the radiations from radioactive elements is the cause of the color of most specimens of smoky quartz. The latter are decolorized by heat because of the reoxidation of the silicon. Coolidge and Moore[10] have radiated vitreous silica with Coolidge's powerful electron-stream and find that the coloration forms a pattern reminiscent of the outline of the fragments from which the glass was made. Either the original crystalline structure tends to be preserved after fusion or the original impurities are an essential factor in the depth of coloration.

Silica and gases. It has been known for some years that vitreous silica is permeable to hydrogen and helium at red temperatures or higher and its permeability at room temperature has been suspected. Elsey[11] has now shown directly that a measurable amount of helium escapes in a few hours under 100 atmospheres' pressure. No escape of hydrogen could be detected in 11 days. This parallels Williams and Ferguson's[12] observations that although hydrogen and helium have about the same solubility in vitreous silica at 500°, helium passes through about 22 times as fast as hydrogen.

Benton and Williams[13] find no evidence for an alleged differential adsorption of CO by vitreous silica from a mixture with oxygen.

Alumina. The structures of both forms of Al_2O_3 have been accurately determined; namely, the natural alpha or corundum form,[14] and the beta,[15] which is known only as an artificial product. The beta form will be found useful in X-ray research because of its large grating-constant.[16]

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[8] See various papers in *Phys. Rev.*, 1926-1927.

[9] *Am. Mineral.*, 10, 203 (1925).

[10] *J. Franklin Inst.*, 202, 722 (1926).

[11] *J. Am. Chem. Soc.*, 48, 1600 (1926).

[12] *J. Am. Chem. Soc.*, 46, 635 (1924).

[13] *J. Phys. Chem.*, 30, 1487 (1926).

[14] Pauling and Hendricks, *J. Am. Chem. Soc.*, 47, 787 (1925).

[15] Hendricks and Pauling, *Z. Krist.*, 64, 303 (1926); Pauling and Björkeson, *Proc. Nat. Acad. Sci.*, 11, 445 (1925).

[16] The only practical difficulty is that of finding large crystals which are not twinned. (Note added by reviewer.)

The average atomic heat capacity of alpha-Al_2O_3 at low temperatures is unusually small, according to measurements by Parks and Kelley.[17] This correlates with the high degree of hardness of the oxide.

There have been several investigations on the action of Al_2O_3 as a catalyst for organic reactions. (See Chap. VI.)

Magnesia. The heat capacity of MgO at low temperatures (94 to 291°K) increases with temperature in the manner characteristic of isometric elements and salts.[17]

The manufacture of articles of pure MgO for laboratory use is described by Mehl, Whitten and Smith,[18] and by Jordan, Peterson and Phelps.[19] A general review of the properties of MgO as made and used in magnesia cements is contributed by Ralston, Pike and Duschak.[20]

Lime. Schumacher[21] has confirmed Kanolt's melting-point (2570°) for CaO, finding the average value 2576°C. from 21 determinations on 2 specimens.

Much useful information on the properties of CaO as made industrially is contained in the papers presented at a Symposium on Lime conducted by the American Chemical Society.[22]

The heat capacity of CaO at low temperatures changes in the same manner as that of MgO.[17]

Calcium Carbonate. Some confusion has been caused in the classification of the forms of $CaCO_3$ by the fact that the so-called "vaterite" differs in constitution according to its method of preparation.[23] There are only 3 forms of $CaCO_3$ at atmospheric temperatures, namely: calcite, aragonite and μ-$CaCO_3$. Vaterite is sometimes spherulitic calcite, sometimes μ-$CaCO_3$.

From the heat of transition of aragonite to calcite (as measured through heats of solution) and their heat-capacity curves, Bäckström[24] concludes that the transition temperature between these two forms must be near 0°K at atmospheric pressure. Under all conditions met with near the earth's surface, aragonite is unstable with respect to calcite.

The System Al_2O_3 : CaO. Studies of the hydration of the four calcium aluminates, and of their reactions with the sulfates of sodium and magnesium in natural waters, have been carried on by Thorvaldson, Harris and Wolochow,[25] and G. R. Shelton [26] at the University of Saskatchewan. The problems are important in connection with the setting of portland cement and its disintegration by the sulfate ground-waters of the Northwest.

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[17] *J. Phys. Chem.*, **30**, 47 (1926).

[18] *Ind. Eng. Chem.*, **17**, 1171 (1925).

[19] *Trans. Am. Electrochem. Soc.*, **50**, preprint (1926).

[20] U. S. Bur. Mines, Bull. 236, 1925.

[21] *J. Am. Chem. Soc.*, **48**, 396 (1926). The melting-points of BaO (1923°) and SrO (2430°) were also determined.

[22] *Ind. Eng. Chem.*, **19**, 550 (1927).

[23] Gibson, Wyckoff and Merwin, *Am. J. Sci.*, **10**, 325 (1925).

[24] *J. Am. Chem. Soc.*, **47**, 2432 (1925).

The System Fe: O. Investigations of this system have been continued at the Bureau of Mines, the University of California, the Geophysical Laboratory, the Rockefeller Institute, the Fixed Nitrogen Laboratory and elsewhere. Fe_2O_3, Fe_3O_4 and FeO are the principal compounds in the system. Sosman and Hostetter's assumption [27] of limited solid solution of Fe_3O_4 in Fe_2O_3 is questioned by Gruner [28] and by some European investigators, on the ground that it is not shown in certain natural ores containing ferrous iron. The case is not a perfectly plain one, because the decrease in oxygen pressure in equilibrium with the oxides from Fe_2O_3 toward Fe_3O_4 is small and is brought out only by a logarithmic plot but it is undoubtedly present and there is as yet no proof that it can be due to any other cause than solid solution.

Gruner finds widely differing rates of oxidation of Fe_3O_4 to Fe_2O_3 depending upon the origin of the Fe_3O_4, and cites interesting cases of the persistence of original hematite patterns in Fe_3O_4 produced from Fe_2O_3.

The structure of the hematite form of Fe_2O_3, as determined by Pauling and Hendricks,[29] is very closely similar to that of the alpha (corundum) form of Al_2O_3. Its average atomic heat capacity [17] at 90° to 290°K is considerably higher than that of Al_2O_3.

Several papers have appeared on the interesting *ferromagnetic modification of* Fe_2O_3, which I shall call "Fe_2O_3 *f*," and which is produced when Fe_3O_4 is oxidized at not too high a temperature. Sosman and Posnjak [30] have found this modification occurring as a natural mineral and have also prepared it in a radically different way, by the dehydration of lepidocrocite, which is one of the two persistent crystalline modifications of the hydrate $Fe_2O_3 \cdot H_2O$. The other and more common modification of $Fe_2O_3 \cdot H_2O$, called goethite, dehydrates to form ordinary paramagnetic Fe_2O_3 or "Fe_2O_3 *p*" (hematite).

[25] *Ind. Eng. Chem.*, 17, 467 (1925).
[26] *Ind. Eng. Chem.*, 17, 589, 1267 (1925).
[27] *J. Am. Chem. Soc.*, 38, 807 (1916).
[28] *Econ. Geol.*, 21, 375 (1926).
[29] See p. 123.
[30] *J. Wash. Acad. Sci.*, 15, 329 (1925).

Fe_2O_3 *f* and Fe_2O_3 *p* differ in color,[30] in biological catalytic activity[31] and in X-ray powder pattern.[30]

On the other hand, Fe_2O_3 *f* gives an X-ray pattern which appears identical with that of the Fe_3O_4 from which it was prepared.[30, 32] Differences in magnetic permeability and hysteresis between different preparations of Fe_3O_4 or of Fe_3O_4 partly oxidized to Fe_2O_3 *f* tend to be eliminated by annealing[33] at 1000°.

Welo and Baudisch's tentative hypotheses as to the placing of the added oxygen atoms in Fe_2O_3 *f* have been tested by Twenhofel[34] by means of X-ray diffraction and have been found untenable. Twenhofel considers this oxygen to be in undefined or haphazard positions, so that it yields no regular diffraction pattern.

The measurement of the heat capacity of natural Fe_3O_4 at low temperatures[17] reveals an absorption of heat at about 115°K suggestive either of a polymorphous crystalline inversion or, at least, of a magnetic inversion.

The prediction[35] that FeO would be found stable only at high temperatures has been borne out by the results of several investigations[36] on the systems Fe : C : O and Fe : H : O. The temperature below which FeO dissociates into Fe and Fe_3O_4 is estimated to be about 570°. By rapid cooling, however, it can be obtained at room temperature.

The structure of FeO so prepared has been determined by Wyckoff and Crittenden[37] as the face-centered cubic, similar to MgO and NaCl. The dimensions are almost identical with those of MgO.

From his experiments on FeO at temperatures above 600°, Ferguson[38] suspects that there may be a ferromagnetic modification of FeO just as there is of Fe_2O_3. FeO as usually prepared is paramagnetic, with a susceptibility less than 0.0005 (Sosman, in [37]).

The evidence on the solubility of FeO or Fe_3O_4 in crystalline Fe has been conflicting. A possible explanation for some of the discrepancies may be found in Almquist and Black's experiments[39] on the poisoning of ammonia catalysts by oxygen, in which they found that very dilute oxygen combines with the catalytically active iron atoms while leaving untouched those atoms which are more stably set in the iron crystal-lattice.

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[31] Welo and Baudisch, *Science*, **62**, 311 (1925); *J. Biol. Chem.*, **65**, 215 (1925).

[32] Welo and Baudisch, *Phil. Mag.*, **50**, 399 (1925). Small differences in spacing have subsequently been found (Sosman and Posjnak, unpublished data).

[33] Welo and Baudisch, *Phil. Mag.*, **3**, 396 (1927).

[34] *Econ. Geol.*, **22**, 180 (1927).

[35] Sosman, *J. Wash. Acad. Sci.*, **7**, 55 (1917).

[36] See especially Eastman and Evans, *J. Am. Chem. Soc.*, **46**, 888 (1924); Ferguson, *Trans. Faraday Soc.*, **21**, 240-242 (1925).

[37] *J. Am. Chem. Soc.*, **47**, 2876 (1925); *Z. Krist.*, **63**, 144 (1926).

[38] *J. Wash. Acad. Sci.*, **15**, 279 (1925).

Silicate systems. For many years it has been assumed that molten silicates, like water solutions of salts, are miscible in all proportions. Suggestions have been made from time to time that differentiation in rock magmas, and perhaps other phenomena, might be explainable by the formation of two non-miscible silicate liquids but there has never been any adequate experimental proof that such relations can exist. Greig[40] has now shown that two liquid layers, one very siliceous and the other much less so, form in the binary systems of SiO_2 with CaO, MgO, SrO, FeO, CoO, NiO, MnO and ZnO. The facts are of considerable metallurgical importance but there is still no evidence that such separations occur in the more complex systems containing Al_2O_3 and the alkalies.

Studies on the structure of diopside[41] ($CaSiO_3 \cdot MgSiO_3$) and of the more complex pyroxenes[42] and also on the relation of chemical to optical properties in the acmitic pyroxenes,[43] are leading toward a better systematized understanding of the relations in the systems $SiO_2 : CaO : MgO$, $SiO_2 : FeO : MgO$, $SiO_2 : CaO :$-$FeO : MgO$, $SiO_2 : Al_2O_3 : CaO : MgO$, and $SiO_2 : Fe_2O_3 : Na_2O$. The amphiboles, forming a corresponding group of silicates similar in composition to the pyroxenes but differing from them in characteristic structural properties, have been studied statistically by Winchell.[44]

The system $SiO_2 : Al_2O_3$. The system $SiO_2 : Al_2O_3$ has excited much interest since the discovery by Bowen and Greig[45] that the stable high-temperature compound in this system is not sillimanite, $SiO_2 . Al_2O_3$, as had formerly been supposed, but a new compound $2SiO_2 . 3Al_2O_3$, subsequently found in nature[46] and named *mullite*. The name "sillimanite" has been appearing frequently in the literature of refractories, in hopeless confusion of meaning as between these two compounds. True sillimanite, and also andalusite and kyanite (which are natural minerals of the formula $SiO_2.Al_2O_3$), all decompose at bright red temperatures to form mullite and silica.[47] Recent patent decisions,[48] following voluminous testimony concerning these compounds, may have far-reaching effects in the silica-alumina refractories industry.

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[39] *J. Am. Chem. Soc.*, **48**, 2814, 2820 (1926).

[40] *Am. J. Sci.*, (5) **13**, 1, 133 (1927).

[41] Wyckoff and Merwin, *Am. J. Sci.*, **9**, 379 (1925).

[42] Wyckoff, Merwin and Washington, *Am. J. Sci.*, **10**, 383 (1925).

[43] Washington and Merwin, *Am. Mineral.*, **12**, 233-252 (1927).

[44] *Am. J. Sci.*, **7**, 287 (1924); *Am. Mineral.*, **10**, 335 (1925).

[45] *J. Am. Ceram. Soc.*, **7**, 238 (1924).

[46] Bowen, Greig and Zies, *J. Wash. Acad. Sci.*, **14**, 183 (1924).

An interesting feature has been the apparent identity of X-ray pattern between the two compounds,[49] which has led some investigators (Eitel, J. T. Norton and others) to assert that the two are not in fact distinct compounds. Improvement of technique has subsequently brought out small differences in the patterns, principally a slight difference in the spacing of the lines.

The system $SiO_2 : Al_2O_3 : CaO$. Investigators in the Portland Cement Association Fellowship at the Bureau of Standards have studied mixtures in the vicinity of the composition $8CaO . Al_2O_3 . 2SiO_2$, which has been asserted by Jänecke,[50] Dyckerhoff[51] and others to be a true compound. Some cooperative work with Dyckerhoff at the Bureau has confirmed the original conclusion of Rankin and Wright that no such compound exists in the equilibrium diagram.[52]

The chemistry of portland cement is stressed by an engineer, in Merriman's[53] proposal that the lime-silica index be given a prominent place in specifications.

The system $SiO_2 : CaO : Fe_2O_3$. By means of experiments at 1200° to 1430°, Hansen and Bogue[54] have outlined the fields in which the compounds $2CaO . SiO_2$, $3CaO . SiO_2$, $2CaO . Fe_2O_3$ and $CaO . Fe_2O_3$ are in equilibrium at the completion of crystallization, in the high-lime part of the system $SiO_2 : CaO : Fe_2O_3$. No evidence of solid solution or of any ternary compound was found. The dusting of $2CaO . SiO_2$ ($\beta - \gamma$ inversion) is prevented only by relatively large amounts of Fe_2O_3. Only a subordinate part of the iron in portland cement clinker is present in the form of calcium ferrites.

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[47] Greig, *J. Am. Ceram. Soc.*, **8**, 465 (1925); *Am. J. Sci.*, (5) **11**, 1 (1926).

[48] Riddle vs. Jeffery and Montgomery; Riddle vs. Locke; Patent Appeal Docket nos. 1853, 1886 (Interferences nos. 46659, 46658), 1925.

[49] Wyckoff, Greig and Bowen, *Amer. J. Sci.*, **11**, 459 (1926).

[50] *Z. Elektrochem.*, **32**, 354 (1926).

[51] Ueber den Verlauf der Mineralbildung, etc., Leipzig, 1925.

[52] Hansen, Dyckerhoff, Ashton and Bogue, *J. Phys. Chem.*, **31**, 607 (1927).

[53] *Eng. News-Rec.*, **96**, 648 (1926).

[54] *J. Am. Chem. Soc.*, **48**, 1261 (1926).

Chapter XIV.

Analytical Chemistry of the Common Metals.

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The metals are considered, so far as practicable, in groups acording to the periodic classification.

Alkali Metals. The well-known indirect method of determining sodium and potassium from the weight of mixed chlorides and the weight of chlorine, has been tested very thoroughly by Neidig and Bollen.[1] The average error in more than fifty determinations varying in the proportion of sodium to potassium and in the total weight of chlorides, was somewhat less than one milligram.

Copper. Brown [2] has developed a modified electrolytic method of separating metals, using an auxiliary electrode of the metal to be deposited. By carefully controlling the potential, he has succeeded in separating copper from tin. Other separations by the same method include bismuth from lead (a difficult separation by other methods), antimony from tin and tin from cadmium. Buehrer and Schupp [3] have devised an interesting potentiometric determination of both copper and iron, particularly useful in analyzing metallurgical products. The metals in solution are reduced by an unstandardized chromous chloride solution and titrated with standard dichromate. Plotting potential and volume of dichromate solution, very sharp breaks in the curve show at the points where each metal is completely oxidized. The excess of chromous chloride is first oxidized, then copper and finally iron.

Magnesium and Calcium. A qualitative separation of magnesium from the alkalies (giving approximate quantitative results) has been developed by Otto.[4] The metals are converted to the nitrates and ignited. Extraction with water and ammonia leaves magnesia undissolved. According to Schoch,[5] magnesium and calcium can be determined volumetrically in water analysis. Using thymolphthalein as indicator, magnesium ion is determined by titrating with standard calcium hydroxide and calcium with a standard solution of sodium carbonate. Sampson[6] has investigated the conditions under which the Macallum microchemical test for calcium (with purpurin) gives satisfactory results. The method is particularly adapted for detecting calcium in tissues. Foote and Bradley[7] have shown that calcium may be determined accurately as the carbonate by igniting the oxalate in a current of carbon dioxide under suitable temperature control. The method gives results fully as good as the method depending on the conversion of the oxalate to oxide. It has the advantages over the oxide method that the carbonate does not change weight in the air and the precipitate of oxalate can be filtered on a porcelain Gooch crucible, saving time in filtration and avoiding the use of platinum for ignition.

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[1] *Ind. Eng. Chem.*, **19**, 154 (1927).
[2] *J. Am. Chem. Soc.*, **48**, 582 (1926).
[3] *Ind. Eng. Chem.*, **18**, 121 (1926).
[4] *J. Am. Chem. Soc.*, **48**, 3016 (1926).

Bailar[8] has devised two methods for the determination of calcium oxide in commercial lime, one depending on titration with standard iodine solution, the other on titration with zinc chloride. The results compare well with those obtained by the standard sucrose method. A thermochemical method for determining magnesium and calcium hydroxides in hydrated limes has been proposed by Richardson.[9] The method depends on the fact that magnesium hydroxide has a much higher dissociation pressure curve than calcium hydroxide, and by determining loss in weight on heating as a function of temperature, the amount of each hydrate present can be determined with some accuracy. The reviewer is not entirely convinced that the method may not be complicated and rendered uncertain by the formation of solid solutions (or by adsorption) between the two hydroxides.

Barium. Various methods for the evaluation of commercial barium dioxide have been tested by Wagner.[10] The most reliable consists in titrating the sample with standard permanganate in a solution of hydrochloric acid containing phosphoric acid and manganese chloride.

Zinc. An ingenious modification of the volumetric ferrocyanide method for zinc has been developed by Cone and Cady,[11] involving the use of diphenylbenzidine (or diphenylamine) as an internal indicator. By using a small amount of potassium ferrocyanide, the indicator is oxidized, forming a blue color. At the end of the titration, a drop excess of standard ferrocyanide reduces this colored compound and the end point is recognized by the color change.

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[5] *Ind. Eng. Chem.*, **19**, 112 (1927).
[6] *Science*, **62**, 400 (1925).
[7] *J. Am. Chem. Soc.*, **48**, 676 (1926).
[8] *Ind. Eng. Chem.*, **18**, 389 (1926).
[9] *Ind. Eng. Chem.*, **19**, 625 (1927).
[10] *Ind. Eng. Chem.*, **17**, 972 (1925).

Cadmium. A delicate test for cadmium in the presence of copper, according to Karns,[12] consists in adding ammonium chloride and a saturated solution of sodium bicarbonate to the mixed chlorides of the two metals. Cadmium precipitates as the carbonate. The test detects as little as 0.1 mg. per cubic centimeter in the presence of five times that amount of copper.

Mercury. The use of mercury at high temperatures has brought up the question of poisoning by mercury vapor, and a new method for detecting mercury vapor in air of quite extraordinary sensitivity has been discovered by Nordlander.[13] The method is based on the reaction between selenium sulfide and the vapor. The sulfide is applied as a coating to paper and turns black when exposed to the vapor. The color produced is a function of time, concentration of mercury vapor and other factors which can be controlled. The lower limit of sensitivity is not known but one volume of mercury vapor in twenty million volumes of air has been detected. In a subsequent article,[14] the same writer shows that the methods used by Turner for determining mercury vapor in air were extremely inaccurate, less than 1/1000th of the mercury actually present being found in some cases, so that Turner's conclusions regarding poisoning from mercury vapor will have to be revised. A sensitive method for detecting mercury in solution has been described by Booth and Schreiber.[15] The common test by amalgamating a copper wire is modified by using a platinum wire anode and fine copper wire cathode and passing a current. The mercury can be detected on the copper by means of a microscope. By concentrating solutions before testing, one part of mercury in a billion parts of water could be detected. An accurate method for determining small amounts of mercury in organic matter has been described by Booth, Schreiber and Zwick.[16] The method is too involved to be described in this place but using 5 mg. or less of mercury, the error in determining was of the order of 0.02 mg.

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[11] *J. Am. Chem. Soc.*, **49**, 356 (1927).
[12] *J. Am. Chem. Soc.*, **48**, 2626 (1926).
[13] *Ind. Eng. Chem.*, **19**, 518 (1927).
[14] *Ind. Eng. Chem.*, **19**, 522 (1927).
[15] *J. Am. Chem. Soc.*, **47**, 2625 (1925).
[16] *J. Am. Chem. Soc.*, **48**, 1815 (1926).

Aluminium. A method for detecting and approximately estimating aluminium in alloys containing less than 0.1% of this element has been described by Lundell and Knowles.[17] The method involves the use of aurintricarboxyllic acid recently mentioned by Hammett and Sottery. The test appears to be reliable even when the alloy contains less than 0.01% of aluminium. A slight modification of the cobalt test for aluminium has been suggested by Otto.[18] Estill and Nugent[19] recommend a confirmatory test for aluminium by means of the colored lake obtained when the hydroxide is precipitated in the presence of tincture of alkanet root. Germuth[20] uses a volumetric method for determining aluminium in its salts. The hydroxide is dissolved in standard sulfuric acid and the excess of the latter is titrated with standard potassium hydroxide, using methyl orange as indicator.

Lead. Scott[21] has proposed a modification of the chromate-iodide method for lead which obviates the use of potassium iodide. The lead chromate is dissolved in hydrochloric acid and treated with a measured excess of standard ferrous sulfate, the excess of the latter being determined with standard dichromate. Diphenylamine is used as internal indicator, the change in color from green to blue, owing to the oxidation of the indicator, serving as the end point. A method of determining metallic lead in pigments and metallurgical products containing lead compounds has been published by McIntosh.[22] He finds that compounds of lead (except the sulfide) are soluble in caustic soda while the metal and some lead sulfide are insoluble. By treating the insoluble residue with a solution of silver nitrate, the metal alone dissolves leaving lead sulfide. The former can then be determined by a volumetric method. To the reviewer it appears very doubtful, in view of the relative solubilities of silver sulfide and lead sulfide, that lead sulfide would not be attacked by silver nitrate, but the action may be sufficiently slow to make the method workable.

Arsenic. The conditions necessary in precipitating arsenic as NH_4MgAsO_4 and determining it as $Mg_2As_2O_7$ have been investigated by McNabb.[23] He finds in particular that the temperature of ignition is important. Excellent results are obtained by heating at 500-600°, while at 900°, the results are low due to volatilization. To determine traces of arsenic in steel, Cameron[24] recommends distilling it from the solution in hydrochloric acid, neutralizing the distillate and titrating with standard iodine.

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[17] *Ind. Eng. Chem.*, 18, 60 (1926).
[18] *J. Am. Chem. Soc.*, 48, 1604 (1926).
[19] *J. Am. Chem. Soc.*, 48, 168 (1926).
[20] *Ind. Eng. Chem.*, 19, 144 (1927).
[21] *Ind. Eng. Chem.*, 17, 678 (1925).
[22] *Ind. Eng. Chem.*, 18, 1320 (1926).
[23] *J. Am. Chem. Soc.*, 49, 1451 (1927).

Bismuth. To determine traces of bismuth in copper, a colorimetric method gives excellent results, according to Jones and Frost.[25] The method depends on freeing the bismuth from other metals and converting to the sulfate. The solution is then treated with potassium iodide and sulfur dioxide and the color compared with that of a standard bismuth solution.

Manganese. For determining traces of manganese, particularly in iron ores, Park[26] recommends modifying the usual bismuthate method by substituting sulfuric acid for nitric acid. Epperson[27] has found, in analyzing limestones, where it is desirable to precipitate traces of manganese with the iron and alumina, that the use of ammonium persulfate when precipitating with ammonia accomplishes this object and does not precipitate calcium. The reviewer fails to see the advantage of this reagent over bromine for the same purpose.

Iron. Burdick[28] has shown that in using the Jones reductor for iron determinations the effect of allowing air to reach the granulated zinc, presumably forming hydrogen peroxide, is entirely negligible, so that the precaution of keeping the zinc out of contact with the air is entirely unnecessary. To determine ferrous iron in solution, Bonner and Yost[29] add sodium phosphate and a measured excess of standard sodium hypochlorite. Potassium iodide is added to liberate iodine by reacting with the excess of hypochlorite. The complex iron phosphate in solution prevents the reverse formation of ferrous iron (by the reaction between ferric iron and potassium iodide) which would, if it occurred, liberate more iodine. The iodine equivalent to the excess of hypochlorite is determined by means of thiosulfate. Good results were obtained by the method, but its drawback lies in the fact that standard hypochlorite changes its strength. To the reviewer it seems that if this method works well, it ought to be possible to do away with the standard solution of hypochlorite entirely, and titrate directly with standard iodine, or with an excess of iodine and thiosulfate. Certainly if the complex formation in solution is sufficient to prevent the formation of ferrous iron in the first case, when an iodide is added, the iron should oxidize completely with iodine in the second. Possibly, also, some other complex would be more efficient, such as a fluoride, a citrate or a borate, or a mixture of them. In place of the usual method for determining ferrous iron in silicates, by titrating with permanganate after solution in hydrofluoric and sulfuric acids, Sarver [30] recommends titration with standard dichromate after the silicate is dissolved, using diphenylamine as an internal indicator. Hopkins [31] calls attention to the fact that colorimetric standards are themselves a source of error in determining small amounts of iron in water analysis. Finally a method may be mentioned for the determination of ferrous, ferric and metallic iron in mixtures of the three, which is proposed by Ingeberg.[32] By determining total iron, ferric iron and chlorine equivalent to metal and ferrous iron, the amount of each can be calculated.

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[24] *Ind. Eng. Chem.*, **17**, 965 (1925).
[25] *Ind. Eng. Chem.*, **18**, 596 (1926).
[26] *Ind. Eng. Chem.*, **18**, 597 (1926).
[27] *Ind. Eng. Chem.*, **17**, 744 (1925).
[28] *J. Am. Chem. Soc.*, **48**, 1179 (1926).
[29] *Ind. Eng. Chem.*, **18**, 55 (1926).

RESEARCH SUGGESTIONS

Following are several suggestions for future work in analytical chemistry:

1. A good method for determining fluorine. All the existing methods are inaccurate or troublesome or both.
2 The gravimetric method for sulfates (by precipitating $BaSO_4$) is surprisingly inaccurate, due largely to adsorption of impurities. Preventing this adsorption or developing any other good gravimetric or volumetric method for sulfates would be extremely valuable.
3. The separation of bismuth and lead as sulfates is extremely unsatisfactory. A study of their solubilities in varying concentrations of sulfuric acid at different temperatures, would not improbably give the key to a satisfactory separation.
4. Tests for, and methods of determining, extremely small amounts of certain elements in the presence of a large excess of others are becoming increasingly important. For instance, certain physical properties of lead probably vary greatly (perhaps to the extent of 100%) in the presence of exceedingly minute amounts of silver. Can the presence of 0.001% of silver in lead be detected, and can it be determined? Similarly, a trace of oxygen (as cuprous oxide) in copper affects the properties of the latter. How can the cuprous oxide be determined?

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[30] *J. Am. Chem. Soc.*, **49**, 1472 (1927).
[31] *Ind. Eng. Chem.*, **17**, 832 (1925).
[32] *Ind. Eng. Chem.*, **17**, 1261 (1925).

Chapter XV.

Inorganic and Analytical Chemistry of Silver, Gold and the Platinum Metals.*

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The precious metals, especially the elements of the platinum group, have received relatively little attention from chemists in the United States in the past two years. This is regrettable as there is ample opportunity for research work of interest and importance. The varied chemical behavior of the elements of the eighth group offers practically a virgin field for the inorganic and the analytical chemist, not to speak of their fellows in other branches of the science. The high cost of these metals has undoubtedly had much to do with the paucity of work done in this field in the laboratories of the universities. Since there need be very little actual loss of material during an extended investigation, major expenses could oftentimes be taken care of by loans, instead of the familiar "grants" so often referred to in the footnotes accompanying scientific papers.

It is suggested that the solubilities of many of the best known salts of the elements of the platinum group might well be determined. Except for a few salts of platinum, solubility data are almost entirely lacking. For those who would study molecular structure there is ample selection of interesting types of compounds. The rapidly extending application in commercial alloys of the erstwhile little used elements of the group, ruthenium, osmium, and rhodium, is causing a real demand on the analyst for more accurate and more rapid methods of analysis. This will be made more acute if the proposed National Stamping Law for platinum is enacted. But it is to be hoped that those who venture in this field of worth-while endeavor will be content to make haste slowly, making very sure of each step. The six platinum elements of the eighth group and their neighbors of the first group, silver and gold, are exceptionally gregarious and do not take kindly to separations. And there are already enough published "methods" which will lead astray the chemist who is called upon to make an occasional platinum metal analysis.

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To suggest one specific project, the writer would like to see someone make a direct determination of the combining weight of osmium with oxygen in osmium tetroxide. This compound is easily made and is reasonably stable but is not so easily handled for weighing. This work would supplement the as yet unpublished determinations by Gilchrist of the ratios $(NH_4)_2OsCl_6$ and $(NH_4)_2OsBr_6$ to Os. The atomic weight of ruthenium might well be redetermined also.

In the following review no reference is made to the numerous articles and patents on processes of extraction and recovery of the metals as these are mostly not of chemical interest. With one possible exception the published references to the part played by these metals in colloid phenomena and catalysis are not reviewed. To make a definite beginning, the line of publication not earlier than July, 1925, is rather sharply drawn.

Silver. Trivelli and Sheppard[1] observed microscopically the decomposition by light of specially prepared silver bromide crystals and of the silver bromide grains in photographic emulsions. In the case of the crystals the decomposition occurs in definitely oriented patterns depending upon the growth and structure of the crystal. In the grains of emulsions the decomposition is largely irregular and the visible decomposition does not parallel the developable sensitivity. The authors suggest that the points of decomposition are oriented in the crystal according to the gradients of ionic deformation, or perturbation of electron orbits following certain directions of growth.

Wilsey[2] examined mixed crystals of silver chloride with silver bromide, and of silver bromide with silver iodide, by X-ray analysis. Mixtures of chloride and bromide showed the simple cubic structure of the pure components, the lattice spacing following a linear relation with the molecular concentration of each component. Most of the bromide-iodide mixtures showed the existence of two types of mixed crystals—one the simple cubic of silver bromide with an enlarged lattice spacing, and the other the diamond cubic or hexagonal type of silver iodide, with slightly diminished lattice spacing. Up to 70 molecular % of silver iodide the silver bromide structure predominated in the mixture. It is thought that the enlargement of the silver bromide lattice caused by the presence of silver iodide is related to the increased photographic speed of silver bromide emulsions containing small percentages of silver iodide.

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[1] *J. Phys. Chem.*, **29**, 1568 (1925).
[2] *J. Franklin Inst.*, **200**, 739 (1925).

In connection with the above should be noted the work of Huse and Meulendyke,[3] who observed the spectral sensitivity of silver iodide and mixtures of iodide and bromide. They found that the iodide is sensitive only to wave lengths shorter than 440 mμ. An emulsion containing 30% of silver iodide does not show any break at this point but the break is shown distinctly by mixtures containing 32%, which indicates that at about this point the iodide begins to crystallize separately.

Lambert [4] determined the solubility of silver bromide and potassium bromide in water in contact with both solid salts at temperatures from 30 to 100° at 10° intervals. At 100° the solution contains 48.66% by weight of potassium bromide and 10.55% of silver bromide. The entire system, silver bromide-potassium bromide-water is discussed and a photograph of the model of the system is shown. There are also some data on the system, silver chloride-potassium chloride-water.

Baxter [5] determined the solubility of silver iodate at 75° in pure water and in the presence of potassium perchlorate, nitrate and sulfate, and of magnesium sulfate and barium nitrate, at concentrations ranging from 0.0002 to 0.1 M. The determinations were made primarily to test, and served to confirm, the inter-ionic attraction theory [6] at very small concentrations and the theory of the variation of the activation effect with the temperature and dielectric constant of the solution.

Hill and Miller [7] studied the system, silver perchlorate-toluene-water. The solubility of silver perchlorate in toluene was determined at temperatures from — 73.5°, where it is practically zero, to + 75°, at which point the saturated solution contains 54.60% by

[3] *Phot. J.*, **66**, 306 (1926).

[4] *J. Phys. Chem.*, **30**, 972 (1926).

[5] *J. Am. Chem. Soc.*, **48**, 615 (1926).

[6] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); Debye, *ibid.*, **24**, 334 (1923) and **25**, 97 (1924); Noyes, *J. Am. Chem. Soc.*, **46**, 1080, 1098 (1924).

[7] *J. Am. Chem. Soc.*, **47**, 2702 (1925).

weight of $AgClO_4$. At 25° the solubility is 50.3%. Below 22.6° the solid phase is $AgClO_4 \cdot C_7H_8$. The ternary system, studied from —94 to +91.75°, showed seven quintuple points and twenty four-phase equilibria. The intersection of two binodal curves, shown by the system in addition to the solubility curves for the three solid phases, gives rise to a three-liquid system which is stable from —24.1° to above +90°.

Klosky and Woo[8] measured the solubility at 25°C. of silver oxide in alcohol-water mixtures containing 0 to 91.5% of alcohol by weight. The solubility varies from 26.2 mg. per liter in pure water to 9.1 mg. in 91.5% alcohol, the shape of the solubility curve resembling that of silver nitrate in alcohol-water mixtures. The determinations were made nephelometrically.

Beckley and Taylor[9] determined the adsorption of various silver salts by silver iodide and found the following order, beginning with the highest adsorption: benzoate, acetate, nitrite, bromate, naphthalenesulfonate, benzenesulfonate, nitrate, chlorate, ethylsulfate and perchlorate. They point out that the less soluble salts are strongly adsorbed and the more soluble ones weakly adsorbed, although the reverse of the order of solubility is not exactly followed.

Colcord, Kern and Mulligan[10] studied the conductivity of electrolytes used in the electrolytic separation of silver and gold, including the effect of the copper content of the electrolyte on the conductivity and the effect of ammonium nitrate on the conductivity and on the characteristics of the silver deposit.

A review of work on silver done in the United States in the past two years should certainly include the work done by Jordan, Grenell and Herschman[11] on the resistance to tarnish and certain physical properties of a large number of silver alloys. The possibility of developing a non-tarnishing silver alloy, preferably of sterling fineness, has been much in the mind of those interested in the silver industry. The authors prepared and studied numerous binary and ternary alloys of silver with base metals and some base metal alloys to which gold also was added. It was found that cadmium-silver and zinc-silver were the most tarnish resistant of the binary alloys but were of the lowest tensile strength of all the workable binary alloys. The addition of antimony or tin, or both, increased the strength and showed some tendency to increase the tarnish resistance. Silver-zinc alloys with tin or antimony or both added, but with a total base metal not exceeding 7.5% (the limit for sterling fineness), produced workable alloys of marked tarnish resistance. Some alloys of satisfactory mechanical properties, but below sterling fineness, were very tarnish resistant but the authors state that none of the alloys studied failed to tarnish under sufficiently severe conditions. Some of these latter alloys contained enough gold to offset the lowered intrinsic value caused by the presence of more than 7.5% of base metal. The paper to which reference is made is preliminary to a more detailed publication which will appear shortly.

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[8] *J. Phys. Chem.*, **30**, 1179 (1926).
[9] *J. Phys. Chem.*, **29**, 942 (1925).
[10] *Trans. Am. Inst. Mining Met. Eng.*, **73**, 108 (1926).
[11] *Mining and Metallurgy*, preprint 1661-E (March, 1927).

Gold. The matter of greatest interest in connection with gold in the past two years has been the much disputed question of the synthesis of gold from mercury. There appears to be but one published contribution from the United States on this subject. Sheldon and Estey [12] reported the results of unsuccessful attempts to confirm Miethe's observations. Experimental details are given. Apart from the great interest of this subject from the standpoint of theoretical chemistry the experimental work done has brought forth as byproducts some very valuable observations on the detection of minute amounts of gold and on the difficulty of removing the last traces of gold and silver from mercury by distillation. Abundant references to these questions are to be found in the issues of Chemical Abstracts for the past two years.

Swanger [13] developed a complete procedure for the analysis of gold alloys used in dentistry. The metals provided for in the scheme are those frequently present in such alloys, viz., gold, silver, platinum, palladium and copper, and the following which were present in small quantities in one or more of some forty commercial alloys: iridium, rhodium, zinc, nickel, tin, manganese, iron and magnesium. Details of the procedure necessary for very high accuracy are given. The refinements which may be omitted if less accuracy is required are indicated in most cases. The paper has tables showing the experimental work done in the development of the methods for the determination of iridium and tin and of the contamination of gold by platinum and palladium when precipitated by sulfur dioxide. The compositions of thirteen typical alloys are also tabulated.

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[12] *Ind. Eng. Chem., News Edition,* **4,** No. 23: 5 (1926).

[13] Bur. Standards, Sci. Papers No. 532 (1926).

Lenher and Kao[14] determined the partition ratios at 20°C. of gold chloride (chloroauric acid) between water and a large number of esters. Ethyl acetate was found to give the best extraction and this in turn from aqueous solutions containing ten per cent of hydrochloric acid. It was found that gold chloride could be separated completely in this way from all of the more common chlorides, the compounds tried being: sodium, potassium, magnesium, barium, ferric, aluminum, strontium, calcium, chromium, manganous, cobalt, nickel, zinc, mercuric, cupric, cadmium, lead, bismuth, antimony and stannic chlorides and arsenic acid.

Roseveare with Buehrer[15] prepared and analyzed pure auric oxide preparatory to a determination of the free energy of this substance which is to be published later. The compound was prepared by barely acidifying with sulfuric acid a solution of gold in aqua regia to which sufficient potassium hydroxide had been added to redissolve the precipitate first formed. To free the product from chlorides and sulfates it was necessary to redissolve in boiling potassium hydroxide solution and reprecipitate with an excess of sulfuric acid, then to repeatedly shake with water and centrifuge. The best method of analysis proved to be to treat a portion of the suspension of hydrated oxide with hydrochloric acid and a measured excess of titanous chloride solution in a carbon dioxide atmosphere, titrating the excess of titanous ion with ferric chloride with potassium thiocyanate as indicator and afterwards weighing the precipitated gold.

Platinum Metals. Gillespie and Hall[16] made a new study of the absorption of hydrogen by palladium black and the possible formation of the compound, Pd_2H. They determined the relation of the volume of hydrogen absorbed to its pressure at 0, 30, 80, 160 and 180°. The authors believe that in the earlier work of Hoitsema[17] on the pressure-composition relation equilibrium was not established, and cite the work of Lambert and Gates[18] on palladium sponge as showing that true equilibrium cannot be reached by operating isothermally. The present authors believe that they attained true equilibrium by reducing the pressure of hydrogen, heating briefly to 360° and then restoring the original temperature. The hydrogen thus driven off was reabsorbed by the palladium and horizontal isotherms over a certain range were obtained at each temperature. In the curves for 160 and 180° the horizontal portion ends sharply at a composition corresponding to Pd_2H. At 80° the break is very slightly beyond this point and at 30 and 0° the horizontal portions extend progressively further. Identical curves were obtained at 0° for palladium black prepared by two different methods.

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[14] *J. Phys. Chem.*, **30**, 126 (1926).
[15] *J. Am. Chem. Soc.*, **49**, 1221 (1927).
[16] *J. Am. Chem. Soc.*, **48**, 1207 (1926).
[17] *Z. physik. Chem.*, **17**, 1 (1895).
[18] *Proc. Roy. Soc.*, **108A**, 456 (1925).

The contributions of Howe and his students to the chemistry of ruthenium were extended by the work of Howe and Haynes[19] on the isomeric chlorides of this element and of Howe and Mercer[20] on the solubility of the metal in alkali hypochlorite solutions. In the former paper it is stated that the alpha series (ordinary pentachlororuthenites) exist as M_2RuCl_5 and $M_2RuCl_5\cdot H_2O$ and that this series may be converted to the beta series, originally called by Howe "aquo-chlororuthenates," by the action of certain organic compounds and reducing agents. The aquo salts are thought to be isomeric with the monohydrated alpha salts but are very different in properties. The dehydrated beta salts are identical with those produced from hexachlororuthenates by the removal of one atom of chlorine. These salts apparently are isomers of the anhydrous alpha salt but are not identical with it. Limited study of the bromo salts indicates behavior similar to that of the chloro salts.

These views are greatly modified in a later (preliminary) article by Howe,[21] who concludes from his own experiments and the observations of Charonnat[22] that the pentachlororuthenite, which always has been supposed to be a salt of tervalent ruthenium, is actually M_2RuCl_5OH, a partially hydrolyzed salt of quadrivalent ruthenium. If the full details of the work substantiate this idea, as seems entirely probable, one of the long standing puzzles in the chemistry of the platinum metals will have been solved. The aquo or beta salt then becomes the true chlororuthenate. It is not yet clear how the "alpha" salt was thought to exist in anhydrous form although this probably dates from the work of Claus (1844).

The results of the work by Howe and Mercer[20] lead the authors to the conclusion that ruthenium and its compounds, if finely divided, are completely soluble in solutions of alkali hypochlorites. When an excess of alkali is present only ruthenates are formed, otherwise some ruthenium tetroxide is formed. This behavior may be used to separate ruthenium from the other platinum metals, except osmium. Ruthenium can be completely distilled as tetroxide from a solution of potassium ruthenate after treatment with chlorine. In the later paper by Howe [21] it is stated that the solution of hydrochloric acid in which the ruthenium tetroxide is collected, and in which the ruthenium reduces to the quadrivalent state, may be titrated with stannous chloride, the ruthenium thus being reduced quantitatively to the tervalent condition.

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[19] *J. Am. Chem. Soc.*, 47, 2920 (1925); *cf.* Briggs, *ibid.*, 48, 2127 (1926); Howe, *ibid.*, 48, 2129 (1926).

[20] *J. Am. Chem. Soc.*, 47, 2926 (1925).

[21] *Science*, 65, 508 (1927).

[22] *Compt. rend.*, 181, 866 (1925).

Oburn, Jr.,[23] published the reactions of chloride solutions of the six platinum metals with the better known inorganic reagents and some eighty odd organic reagents of various classes. Several new color reactions were found which are useful for the qualitative detection of several of the individual metals. Largely based on the results of the foregoing work the author developed a scheme of analysis which may be regarded as semiquantitative. In this scheme the six elements are removed in the following order: palladium with dimethylglyoxime, platinum with α-furildioxime, rhodium with potassium nitrite, ruthenium as hydrated oxide by means of sodium hydroxide, iridium and osmium displaced by hydrogen (zinc plus hydrochloric acid) and osmium separated from this mixture by solution in sodium hypochlorite. Necessary details of the procedure are given in the second paper.

Davis [24] reports on the trial of several methods of assay for the copper-palladium-gold-silver concentrates being produced by the Alaska Palladium Company at Salt Chuck, Prince of Wales Island, Alaska. The procedure which he regards as the best of those tried was as follows: Half assay ton samples were fused with borax glass, sodium carbonate and 90 g. of litharge, covered with borax glass. Silver, as chloride, equivalent to ten times the palladium content was added to the charge. The buttons thus obtained being too brittle, lead was added and the buttons scorified twice singly and then in pairs, followed by a single scorification and then cupellation. Silver was determined in a separate sample.

[23] *J. Am. Chem. Soc.*, 48, 2493, 2507 (1926).

[24] Bureau of Mines, Reports of Investigations No. 2731 (1926).

Chapter XVI.

Inorganic and Analytical Chemistry of the Rare Metals.

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A fair amount of activity in this field, among American chemists, during the period covered by this review, is shown by the following references.

Middleton[1] has studied the action of "Aluminon," the reagent recently applied for the detection of aluminum, on beryllium, thorium, zirconium and the rare earths, and finds that only beryllium interferes with the test, by giving under similar conditions a red lake like that given by aluminum.

Later Corey and Rogers,[2] working on the same general problem, investigated the behavior of scandium, gallium, indium, thallium and germanium, and found that gallium gives results similar to those given by aluminum. It is not surprising that these two elements, which resemble aluminum in many chemical reactions, should give similar results with this reagent.

Dennis[3] and his associates have continued their work on germanium, describing apparatus for the purification and study of the volatile compounds, and discussing the preparation and the properties of the tetrachloride, the tetramethyl and chloroform derivatives and the substitution of GeO_2 for SiO_2 in the formation of glass. A number of glasses were made, and the difference in optical properties makes it probable that they may be employed in the construction of optical systems. These investigations register an important advance in our knowledge of this hitherto little known element.

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[1] *J. Am. Chem. Soc.*, **48**, 2125 (1926).
[2] *J. Am. Chem. Soc.*, **49**, 216 (1927).
[3] *J. Phys. Chem.*, **30**, 1047, 1049, 1055, 1510 (1926).

Baxter and Butler,[4] by analysis of titanium chloride prepared by fractional distillation, arrive at a value of 47.9 for the atomic weight of titanium. This is 0.2 lower than the previously accepted result obtained by Thorp. The well known accuracy of Baxter's work lends confidence to this result.

Thornton and Wood [5] study the standardization of titanous sulfate solutions, and find that Sibley iron ore and ferric alum serve well for primary and secondary standards. They recommend as an inside indicator 5 cc. of a 10% solution of potassium sulfocyanide. They claim that with a carefully set up apparatus of proper design titanous sulfate solution can be kept three months without changing its standard. They recommend the minimum amount of rubber tubing between the storage bottle and the burette.

Brown and Snyder,[6] having in mind the remarkable solvent action of selenium oxychloride, prepared and investigated vanadium oxytrichloride as a solvent. They report results upon 125 substances, finding nearly all inorganic compounds and all metals insoluble, all nonmetals soluble, all purely organic compounds either dissolved or acted upon, organic liquids miscible in all proportions and liquid aldehydes reacted upon vigorously.

Stoppel, Sidener and Brinton [7] find that molybdenum and vanadium are better separated as sulfides by precipitation in a pressure flask than by acidifying an ammoniacal solution which has been saturated with H_2S.

Krauskopf and Swartz,[8] on studying the detection of molybdenum by the formation of red coloration produced by the action of zinc and hydrochloric acid in the presence of potassium sulfocyanide, find that in the presence of no interfering substances the sensitivity of the test is one part in a million. They also find that the ratio between the molybdenum and the sulfur in the thiocyanate radical shows the compound formed to be $Mo(SCN)_3$ rather than $Mo(SCN)_4$. The latter formula is the one which has generally been given to represent the product formed.

Sears [9] has found what seems to be a satisfactory solution of the problem of separating tantalum and columbium, by fusing tantalite and columbite with sodium pyrosulfate at 835-875°, then leaching with water, and washing the residue with 3 *N* hot hydrochloric acid, and finally heating in a steam bath with 1 : 1 sulfuric acid until all evidence of action ceases. After this treatment the tantalum remains unattacked while the columbium is in solution.

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[4] *J. Am. Chem. Soc.*, **48**, 3117 (1926).
[5] *Ind. Eng. Chem.*, **19**, 150 (1927).
[6] *J. Am. Chem. Soc.*, **47**, 2671 (1925).
[7] *Chem. News*, **130**, 353 (1925).
[8] *J. Am. Chem. Soc.*, **48**, 3021 (1926).
[9] *J. Am. Chem. Soc.*, **48**, 343 (1926).

Goggin, Cronin, Fogg and James [10] obtain uranium in a practically pure state by reducing uranous chloride with sublimed metallic calcium.

Lundell and Knowles,[11] investigating the gravimetric determination of uranium by precipitation of $(NH_4)_2U_2O_7$ and conversion into U_3O_8 by ignition, find the result was much helped by the addition of macerated paper. Commenting on the volumetric method by the use of the Jones reductor they recommend a dilute solution of sulfuric acid at a temperature of from 20-25° and that the reduced solution be agitated by passing in a current of pure air for about five minutes. This brings the over-reduced compounds back to the tetravalent condition before treatment with potassium permanganate.

Although selenium and tellurium can hardly be classified among the rare metals, it is possibly not out of place to refer to the recent work of Lenher,[12] who has found that hydroxylamine hydrochloride in hydrochloric, tartaric and citric acid solutions gives a better separation of these elements than hydroxylamine sulfate.

Schrenk [13] has worked out a method for the estimation of tellurium by oxidizing with an excess of potassium dichromate and titrating electrometrically with ferrous sulfate.

Electrometric methods give much promise, and we shall probably hear more of them in the future, both in this field and in that of the common elements.

Ramsey [14] has found that in the iodometric determination of vanadium the catalytic effect of pentavalent vanadium on the oxidation of the iodide ion causes inaccurate results when the process is carried on in the presence of oxygen and he has worked out a method by means of which oxygen may be excluded.

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[10] *Ind. Eng. Chem.*, 18, 114 (1926).
[11] *J. Am. Chem. Soc.*, 47, 2637 (1925).
[12] *J. Am. Chem. Soc.*, 47, 2454 (1925).
[13] *J. Am. Chem. Soc.*, 48, 139 (1926).
[14] *J. Am. Chem. Soc.*, 49, 1138 (1927).

Chapter XVII.

Microchemistry.

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Although it is certain that the use of microchemical tests and determinations has greatly increased in American industrial and research laboratories no such impression is gained by the casual reader of our periodical publications. It is only after a careful scrutiny that one discovers how much microchemical and microscopic work enters into the chemical investigations of today; but the articles are few indeed that appear with a title indicating that the observations and data recorded are chiefly of a microchemical nature.

Although we Americans are probably employing these methods in industrial laboratories more than other nations we are publishing comparatively little upon microchemical apparatus and methods. This is the more surprising since the economic value of this type of chemical investigation is beginning to be fully appreciated.

In compiling this survey of American microchemistry covering the period July, 1925, to July, 1927, the authors believe that microscopy, as such, employed by chemists to solve problems which are fundamentally chemical in their nature must be considered as falling under the general topic—microchemistry.

We have, therefore, striven to find and roughly classify all data and methods involving the use by American chemists of supersensitive chemical methods or microscopy. As regards the latter it should be patent that mere microscopic examinations usually yield information definitely chemical in its nature without the necessity of having recourse to chemical reactions. Since this aspect of microscopy is all too often overlooked by the chemist, we trust that in the data presented in this review the enormous importance of this phase of physico-chemical investigations will be obvious.

Michrochemical Analysis. Gesell and Dittmar[1] have very conclusively shown that in as difficult a field as that of sampling and analyzing crude drugs "micro" methods not only saved time and labor but the results were fully as reliable as those obtained by the usual so-called standard methods.

Similar conclusions were reached by Kemmerer and Hallett[2] in their study of combustion analyses of organic compounds by means of improved Pregl methods.

Chamot[3] has shown how time and labor may be saved by chemical microscopy and that there are few problems to the solution of which microscopic methods cannot be made to contribute.

Keenan[4] has also repeatedly emphasized the importance of microscopic methods and points out the necessity of chemists employing optical-crystallographic methods for the sake of accuracy and economy of time and material.

Booth, Schreiber and Zwick[5] were able to quantitatively determine infinitesimal amounts of mercury in organic matter by destroying the organic matter with permanganate and sulfuric acid, then precipitating and setting free the Hg by heating with $PbCrO_4$. The volume of the Hg was then determined in a special microburette by means of a microscope and from this value the weight was computed.

In order to determine very small amounts of arsenic adhering to fruit sprayed with arsenicals White[6] devised a micro-Gutzeit method which is simple, rapid and accurate.

Nordlander[7] has shown that 1 part of mercury vapor in 8,000,000 can be readily detected by means of selenium sulfide paper.

McHaffie[8] working upon the problem of the detection of water vapor in permanent gases devised a special apparatus whereby he is able to determine as small a quantity as 0.5 mmg. with an accuracy of 1 in 1,000.

Van Slyke[9] has developed a very rapid and fairly accurate gasometric micro-Kjehldahl determination of nitrogen involving the use of the Van Slye-Neill gas apparatus.

Rising and Hicks,[10] taking advantage of solution temperature phenomena, find that it is thus possible to determine very small quantities of water in methanol providing the water does not exceed 4%.

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[1] *Ind. Eng. Chem.*, 17, 808 (1925).
[2] *Ind. Eng. Chem.*, 19, 173 (1927).
[3] *Sci. Monthly*, 24, 366 (1927).
[4] *J. Am. Pharm. Assoc.*, 14, 112 (1925).
[5] *J. Am. Chem. Soc.*, 48, 1815 (1926).
[6] Report Dept. Farms and Markets, State of N. Y., 1926, 80.
[7] *Ind. Eng. Chem.*, 19, 518 (1927).
[8] *J. Am. Chem. Soc.*, 48, 1143 (1926).
[9] *J. Biol. Chem.*, 71, 235 (1927).
[10] *J. Am. Chem. Soc.*, 48, 1929 (1926).

Foulger,[11] studying the colorimetric determination of silicon in tissues by the silicomolybdate method, concludes that the results are accurate even in the presence of phosphates providing that sufficient acetic acid is employed.

According to Krauskopf and Swartz[12] 1 part of molybdenum in 1,000,000 may be detected by the color produced by molybdenum thiocyanate.

Chamot and Cole[13] developed new micro-tests for germanium depending upon the volatility of germanium chloride and the characteristic appearance under the microscope of sodium fluogermanate and rubidium germanomolybdate.

Mason and Chamot[14] report that *m*-phenylenediamine may be employed as a micro-test for bromine, that the test is specific for this halogen and has a sensitivity of about 0.5 μ gram. By proper procedures they have shown that it is possible to differentiate between bromides, hypobromites and bromates.

The microscopic identification and differentiation of compounds by means of their crystallo-optical properties are justly growing in favor. Williams and Lasselle[15] have given data for the identification of creatine; Power and Chestnut[16] for the identification of phytosterol and betain, and Wherry[17] for the differentiation and identification of the crystallizable sugars including *l*-arabinose, fructose, *d*-glucose hydrate, α-lactose hydrate, lyxose, *d*-mannose, *d*-melibiose, raffinose, rhamnose hydrate, *d*-ribose, sucrose, trehalose and *d*-xylose.

One of the most instructive and striking of the applications of these crystallographic methods of identification is to be found in Eagles and Johnson's[18] studies of the compound ergothioneine obtained from the ergot of rye. In the course of this investigation Wherry was able to prove the identity of this crystalline compound with the crystalline sympectothion of Hunter and Eagles and the thiasine of Benedict; both the latter compounds were isolated from pig's blood.

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[11] *J. Am. Chem. Soc.*, **49**, 429 (1927).
[12] *J. Am. Chem. Soc.*, **48**, 3021 (1926).
[13] *Mikrochemie*, **4**, 97 (1926).
[14] *Mikrochemie*, **4**, 145 (1926).
[15] *J. Am. Chem. Soc.*, **48**, 536 (1926).
[16] *J. Am. Chem. Soc.*, **48**, 2721 (1926).
[17] *J. Wash. Acad. Sci.*, **16**, 433 (1926).
[18] *J. Am. Chem. Soc.*, **49**, 575 (1927).

Terry and Miles[19] found microscopic methods useful in their studies of dihydroxydihydroquinone.

French[20] finds that candle scarlet (Geigy) and oil red-O (N. Anil.) are superior to Sudan III in staining fats and oils.

Microscopic Apparatus and Manipulative Methods. Increasing emphasis is being placed on special methods of microscopic illumination, in the examination of transparent preparations as well as in the field of metallography. Leiter[21] and Silverman[22] both employ quartz rods to "conduct" light from the source to the object. Jones[23] describes methods of photographing surfaces of paper under strictly comparable conditions, as a means of recording their lustre, brightness, and texture.

A simplified slit ultramicroscope has been designed by Foster[24] and is now being manufactured in America. Motion photomicrographic studies have been carried out by Kraemer[25] on the setting of gelatin and by France on clays[26] and on the rate of growth of $CuSO_4$ crystals.[27] The latter uses one of the popular amateur cameras attached to a binocular eyepiece serving as a finder.

Considerable work with the "micromanipulator" is being carried out and Taylor[28] has devised a micro-electrode for the study of protoplasm in the individual cell. The A.S.T.M. Committee Report on Microhardness[29] discusses the value and limitations of the scratch method employing the "microcharacter." Plastic flow in suspensions has been investigated quantitatively under the microscope by Green and Haslam.[30]

An exhaustive study of heavy liquids suitable for specific gravity separations by Sullivan[31] gives valuable information for microscopists and other workers with powdered materials.

Observations of Physico-Chemical Properties. Bowen's paper[32] on the inversion of NH_4NO_3 and its binary systems with NH_4Cl and $(NH_4)_2SO_4$ exemplifies very strikingly the possibilities of microscopic methods in phase rule studies. Trivelli and

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[19] *J. Am. Chem. Soc.*, **48**, 2647 (1926).
[20] *Stain Tech.*, **1**, 74-7 (1926).
[21] *J. Optical Soc. Am.*, **11**, 187 (1925).
[22] *Ind. Eng. Chem.*, **17**, 573 (1925).
[23] *Paper Trade J.*, **83**, no. 16, 56 (1926).
[24] Colloid Symposium Monograph, **3**, 296 (1925).
[25] *J. Phys. Chem.*, **29**, 1523 (1925).
[26] *J. Am. Ceram. Soc.*, **9**, 67 (1926).
[27] Colloid Symposium Monograph, **3**, 317 (1925).
[28] *Proc. Soc. Exptl. Biol. Med.*, **23**, 147 (1925).
[29] *Proc. Am. Soc. Testing Materials*, **26**, 572 (1926).
[30] *Ind. Eng. Chem.*, **17**, 726 (1925).
[31] Bur. Mines, Tech. Paper 381, 30 p. (1927).
[32] *J. Phys. Chem.*, **30**, 721 (1926).

Sheppard[33] have observed the effect of light on single grains of silver halide in photographic emulsions. Bartlett[34] describes the changes in microscopic structure of various substances exposed to high powered cathode X-ray tubes. The fineness and stability of emulsions have been studied by Krantz and Gordon.[35] An improved cell for the quantitative ultramicroscopic study of cataphoresis is described by Northrop and Kunitz.[36] Hitchcock[37] has attempted to measure the size of pores in collodion membranes. Nichols and Thies,[38] studying the influence of citrates on the precipitation of $BaSO_4$, conclude that a sub-ultramicroscopic sol is formed. Flocculation and its relation to the plasticity of suspensions have been investigated by Breyer.[39] Structural colors in insects are described by Mason.[40] The growth of large bubbles at the expense of small ones has been followed under the microscope by Baylis,[41] who points out its relationship to the air-binding of sand filters.

Particle size determinations are playing an increasing part in the examination of powdered materials, and microscopic methods are of particular value because of the light thrown upon the shape and physical character of the particles. Nonmicroscopic methods of particle size determination have been checked by microscopic observations by Stutz and Pfund,[42] and by Shafor.[43] Reactions where one constituent is solid are markedly affected by the fineness and surface presented by this material, as is emphasized by Lepsoe[44] in the case of Zn dust used in the cyanide process for gold recovery. Dorr and Bull[45] discuss the relationship between the size of solid particles and the size of the aggregate resulting from their reaction in the causticization of lime.

All too rarely does one note a statement of optical properties accompanying the description of a new substance, and it is perhaps because of the incompleteness of such information that optical crystallographic methods have not been employed to the extent which their usefulness merits.

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[33] *J. Phys. Chem.*, **29**, 1568 (1925).
[34] *J. Chem. Educ.*, **3**, 1369 (1926).
[35] *J. Am. Pharm. Assoc.*, **15**, 83 (1926).
[36] *J. Gen. Physiol.*, **7**, 729 (1925).
[37] *J. Gen. Physiol.*, **9**, 755 (1926).
[38] *J. Am. Chem. Soc.*, **48**, 302 (1926).
[39] *J. Phys. Chem.*, **29**, 1266 (1925).
[40] *J. Phys. Chem.*, **30**, 383 (1926); **31**, 321 (1927).
[41] *Ind. Eng. Chem.*, **17**, 974 (1925).
[42] *Ind. Eng. Chem.*, **19**, 51 (1927).
[43] *Ind. Eng. Chem.*, **19**, 573 (1927).
[44] *Trans. Am. Inst. Mining Met. Eng.*, **71**, 1061 (1925).
[45] *Ind. Eng. Chem.*, **19**, 558 (1927).

Hill [46] gives a method of measuring slopes and angles of crystal faces under the microscope. Crystallographic notes have appeared in connection with studies on Al fluorides,[47] NH_4 monometaphosphate,[48] hydroxyureas and carbamazides,[49] chlorovanillin,[50] alkali azidodithiocarbonates,[51] equilibria in alkali carbonates [52] and fluorescein derivatives.[53] Garard and Colt [54] have reported the separation of monoclinic S from cold C_2H_5OH and its subsequent transformation to the rhombic modification. Crystalline substances have been isolated by Ritter [55] from wood lignin.

Ores, Minerals, Ceramics. The chemist can find good use for the methods used by the petrographer in the preparation of thin sections of hard material. Keyes [56] explains the various operations in detail and suggests bakelite as a permeating medium for friable specimens. Weigel [57] has published a paper on special industrial sands, which includes the microscopic characteristics of their mineral constituents.

The progressive thermal decomposition of oil shales is followed under the microscope at temperatures up to 800°C., by means of Stadnichenko's hot stage.[58, 59, 60]

Microscopic studies of ceramic materials are becoming much more common than in previous years, largely due to the leadership of the Geophysical Laboratory and the Bureau of Standards. The recent lines of investigation of the latter include examinations of furnace refractories and sagger bodies [61] and petrographic and particle size determinations of feldspars.[62] Malinovszky [63] has employed microscopic methods in the quantitative determination of quartz in feldspar. Kraner [64] recommends the microscopic study of electrical porcelain as an indication of its quality. Insley [65] describes the development of mullite and the glaze-body contact in earthenware, while Spurrier[66] has examined terra-cotta for voids and fineness and uniformity of grog.

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[46] *J. Am. Chem. Soc.*, **48**, 651 (1926).
[47] *J. Am. Chem. Soc.*, **48**, 1 (1926).
[48] *J. Am. Chem. Soc.*, **49**, 123 (1927).
[49] *J. Am. Chem. Soc.*, **49**, 266 (1927).
[50] *J. Am. Chem. Soc.*, **49**, 535 (1927).
[51] *J. Am. Chem. Soc.*, **49**, 917 (1927).
[52] *J. Am. Chem. Soc.*, **49**, 1235 (1927).
[53] *J. Am. Chem. Soc.*, **49**, 1272 (1927).
[54] *J. Am. Chem. Soc.*, **49**, 630 (1927).
[55] *Ind. Eng. Chem.*, **19**, 624 (1927).
[56] *Am. J. Sci.*, **10**, 538 (1925).
[57] *Trans. Am. Inst. Mining Met. Eng.*, **73**, 434 (1926).
[58] *J. Optical Soc. Am.*, **10**, 605 (1925).
[59] Geophysical Lab. Paper 563.
[60] *Oil and Gas J.*, **24**, No. 46, 120 (1926).
[61] *Ceramist*, **8**, 285 (1926).
[62] Geller, *Ceramist*, **6**, 708 (1925).
[63] *J. Am. Ceram. Soc.*, **10**, 23 (1927).
[64] *Elec. J.*, **23**, 344 (1926).
[65] *J. Am. Ceram. Soc.*, **10**, 317 (1927).

The system $Na_2O \cdot SiO_2$ — $CaO \cdot SiO_2$ — SiO_2 has been investigated by Morey and Bowen,[67] who use petrographic methods to identify the various phases separating. This method has been applied to the identification of "stones" in glass; a new one is described by Peck.[68] The surface devitrification of fused quartz ware has been shown by Vilbrandt[69] to be due to films of salts deposited in evaporations. The microscopic changes involved in the strengthening process for inside-frosted lamp bulbs are described by Pipkin[70] as consisting of a change from a fissured to a botryoidal surface.

Cement, Lime, Plaster. Gillson and Warren[71] as the result of a preliminary optical study of portland cement have reopened the controversy relative to the chemical constitution of cement clinker and the hydrated products. They report that they have found two compounds neither of which agrees with any one of the three compounds described by Rankin and Wright. One of these two compounds was found in both the clinker and hydrated product.

Shelton[72] has continued his study of portland cement and confirms the work of Shepherd and Rankin. He finds in white portland no 5 : 3 calcium aluminate nor free lime present. As the result of microscopic studies Shelton concludes that solutions of sodium sulfate and of magnesium sulfate are "especially destructive in their action upon crystals of hydrated tricalcium aluminate, regardless of the presence or absence of calcium silicate." Their destructive action is even more marked upon crystals of lime.

Hansen and Bogue,[73] from a study of part of the equilibrium diagram $CaO—Fe_2O_3—SiO_2$, conclude that no ternary compounds of $CaO—Fe_2O_3—SiO_2$ exist in the field studied and further that only part of the ferric oxide in portland cement clinker is present as crystalline $2CaO \cdot Fe_2O_3$ or $CaO \cdot Fe_2O_3$. The presence of $3CaO \cdot SiO_2$ has been confirmed. There is inversion of $2CaO$ — SiO_2 to gamma form on cooling except where the concentration of $2CaO \cdot SiO_2$ is low and that of $CaO \cdot Fe_2O_3$ high.

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[66] *J. Am. Ceram. Soc.*, **9**, 773 (1926).
[67] *J. Soc. Glass Tech.*, **9**, 226 (1925).
[68] *J. Am. Ceram. Soc.*, **9**, 351 (1926).
[69] *Ind. Eng. Chem.*, **17**, 835 (1925).
[70] *Ind. Eng. Chem.*, **18**, 774 (1926).
[71] *J. Am. Ceram. Soc.*, **9**, 783 (1926).
[72] *Ind. Eng. Chem.*, **18**, 854 (1926).
[73] *J. Am. Chem. Soc.*, **48**, 1261 (1926).

Whitman and Davis[74] report that the finer the particle size of lime, the slower the rate of settling of the hydrated product and the higher the rate of reaction to acids. Adams[75] confirms these results and states that decreasing the particle size of the lime increases the plasticity figures of the hydrated product and that the putty volume generally follows the plasticity figures.

According to Gardner,[76] by means of microscopic observations and counts made upon mixtures of gypsum, anhydrite, dolomite and shale in powder form (< 200 mesh > 240 mesh), it is possible to determine at once the amount of anhydrite within 5% of the anhydrite actually present.

Pigments and Paints. Some sort of microscopic examination is employed by most manufacturers or users of pigments and fillers, either as a means of identification or for the determination of the size, shape and distribution of particles. Green and Haslam[77] have investigated the relationship between particle size, degree of flocculation and "yield value" in paints and Rhodes and Fonda[78] have studied the effect of particle size on brightness and opacity.

The surface character of films of color varnishes, and the various defects of lustre and pigment distribution have been found by Bartell and Van Loo[79] to be due largely to vortex action in evaporation.

Rubber. Ultramicroscopic studies and microdissections are being carried on in a number of industrial laboratories, in an attempt to establish the nature of the latex particle and the factors which govern its properties. Clark[80] gives a report of the work of Hauser, in which motion pictures are used to record the brownian movement of latex particles and the evidence of a surface membrane as shown by puncturing them under the microscope by means of a micromanipulator. Sebrell, Park and Martin[81] report that this membrane persists through the evaporation of latex.

Green[82] has used ultraviolet illumination in the study of sulfur distribution in vulcanized latex particles. Sheppard and Eberlin[83] observed the ultramicroscopic cataphoresis of latex particles in connection with their work on electrodeposition of rubber. The

[74] *Ind. Eng. Chem.*, **18**, 118 (1926).
[75] *Ind. Eng. Chem.*, **19**, 589 (1927).
[76] *Proc. Am. Soc. Testing Materials*, **26**, pt. i, 296 (1926).
[77] *Ind. Eng. Chem.*, **19**, 53 (1927).
[78] *Ind. Eng. Chem.*, **18**, 130 (1926).
[79] *Ind. Eng. Chem.*, **17**, 925, 1051 (1925).
[80] *Ind. Eng. Chem.*, **18**, 1131 (1926).
[81] *Ind. Eng. Chem.*, **17**, 1173 (1925).
[82] *Ind. Eng. Chem.*, **17**, 802 (1925).
[83] *Ind. Eng. Chem.*, **17**, 711 (1925).

distribution of carbon black and lamp black in rubber has been studied in microtome sections by Spear and Moore.[84]

Oil and Waxes. Microscopic examination of bearing surfaces has been used in a number of studies on lubrication. Koethen [85] concludes that graphite acts as a filler of irregularities and as an easily abraded buffer between metal surfaces. Gilson [86] and Becker [87] correlate the results of their studies on lubricant films with microscopic observations.

Several investigations on the properties of waxes are in progress, and involve microscopic observations of the solidification and crystal character of their constituents. Padgett, Hefley and Hendricksen [88] point out the effect of viscosity and composition of the solvent on the character of wax crystals separating from it. Buchler and Graves [89] explain the formation of needle crystals on the basis of differences of composition of the melt. The microscopic appearance of oil field emulsions is shown by Dow.[90]

Leather. The methods of the histologist have been employed to good advantage in the study of the changes taking place in the different stages of the tanning process. McLaughlin and O'Flaherty [91] present a very detailed study of the anatomy and physiology of skin. Turley [92] gives a general introduction to the microscopy of tanning, and a full discussion of the microscopic technique employed. Wilson and Daub [93] also discuss methods of preparation and give photomicrographs of a variety of different kinds of leather. They have shown [94] by microscopic means that a number of different types of damage to leather are caused by the action of micro-organisms. Frey [95] describes the nature of the imperfections caused by the mange mite.

Textiles, Paper, Wood. A general discussion of the use and methods of microscopy in the textile industry is given by Hoxie.[96] Johnson [97] also points out the applications of micro projection and photomicrography in the study of fibers and fabrics. Mebane and Vilbrandt[98] have studied the relationship between the structure of the cotton fiber and its stage of development when picked, as affecting its behavior on dyeing. Butterworth[99] shows that "neps" in cotton consist of unripe hairs and fragments of seed coats. Textus[100] explains the "fulling" of wool on the basis of microscopic observations. Properties of artificial silks useful for their differentiation are given by Mullin.[101]

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[84] *Ind. Eng. Chem.*, **17**, 936 (1925).
[85] *Ind. Eng. Chem.*, **18**, 497 (1926).
[86] *Ind. Eng. Chem.*, **18**, 467 (1926).
[87] *Ind. Eng. Chem.*, **18**, 471 (1926).
[88] *Ind. Eng. Chem.*, **18**, 832 (1926).
[89] *Ind. Eng. Chem.*, **19**, 718 (1927).
[90] Bur. Mines, Bull. **250**, 1926.
[91] *J. Am. Leather Chem. Assoc.*, **21**, 338 (1926).
[92] *J. Am. Leather Chem. Assoc.*, **21**, 117 (1926).
[93] *J. Am. Leather Chem. Assoc.*, **21**, 193 (1926).
[94] *Ind. Eng. Chem.*, **17**, 700 (1925).
[95] *J. Am. Leather Chem. Assoc.*, **20**, 373 (1925).
[96] *Textile World*, **68**, 3087 (1925).
[97] *Am. Dyestuff Rept.*, **14**, 209 (1925).

The technique of staining papers for analysis, using a modification of Herzberg's stain, is given by Bentzen.[102] Browne and Truax[103] show by a microscopic study that adhesion rather than mechanical interlocking is the chief factor in the strength of glue joints in wood and Weinstein[104] gives methods for the examination of the structure of such joints.

Food, Drugs. The microscope is still the method *par excellence* for the detection of much of the adulteration which may be met with in most of our foods and drugs. In fact microscopic methods are in a large majority of cases the only available means for the detection of foreign material. The present review deals in no way with those results which are based upon the histology of vegetable and animal tissues, but only with the methods and the results of micro-chemistry or chemical microscopy.

Tiny, hard, sandy crystals are formed or often occur in many food products. The consumer is apt to consider such foods unpalatable, or suspect that they contain powdered glass, or other foreign materials. Among the American investigations of problems of this character we find that the crystals frequently met with in canned salmon are magnesium ammonium phosphate (Clark and Clough).[105] Hunziker and Nissen[106] have made careful microscopic studies of the character of lactose crystals in sweetened condensed milk and of the conditions which govern the formation of these crystals. They find that the crystals found in sweetened condensed milk are pure lactose and not mixed crystals of sucrose and lactose.

A large amount of work has been done upon the microscopy of milk, cream and ice cream, almost none of which has as yet been published.[107, 108]

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[98] *Am. Dyestuff Rept.*, **15**, 279 (1926).
[99] *Textile World*, **67**, 3867 (1925).
[100] *Textile World*, **71**, 1423 (1927).
[101] *Am. Dyestuff Rept.*, **16**, 145 (1927).
[102] *Paper Trade J.*, **84**, no. 9, 49 (1927).
[103] Colloid Symposium Monograph, **4**, 258 (1926).
[104] Colloid Symposium Monograph, **4**, 270 (1926).
[105] *Pacific Fisherman*, **23**, 11 (1925); Special Bull., Nat. Canners Assoc., Northwest Branch, 1925.
[106] *J. Dairy Sci.*, **9**, 517 (1926); **10**, 139 (1927).

Alsberg and Perry[109] and Alsberg[110] have continued work upon starch and its gelatinization. The conclusion is reached that starch is crystalline. Naudain[111] advances the idea that a large proportion of small starch granules in a flour indicates a good grade of flour relative to its baking quality.

Keenan and Hann,[112] discussing Baly's alleged photosynthesis of coniine, point out that the identification of this alkaloid by means of the optical constants of its crystallizable salts is by no means as difficult and uncertain as by chemical tests. The optical constants of coniine hydrochloride are given in detail.

Keenan[113] has shown that by the microscopic examination of commercial samples of reduced iron it is possible to differentiate between good and bad samples and to detect samples which do not conform to the U. S. P. Standard.

Metals and Alloys. The methods and principles involved in the microscopic study of metals are of interest on other grounds than their metallurgical applications. Remarkable refinements in microscopical technique are being made available for all sorts of opaque materials, and the interpretation of the behavior of binary and ternary systems in general bears close relationship to the phenomena being studied by the metallographer. Campbell[114] emphasizes the application of metallographic methods to non-metallic systems of sulfides and silicates, as well as discussing the more general aspects of metallography.

Pirk[115] discusses the technique of preparing and examining metals microscopically, and the recent edition of Sauveur[116] contains much valuable information on methods applicable to materials other than the ferrous alloys. The recent tendency toward very high magnifications, of which Lucas[117] is the chief exponent, calls for the utmost perfection in the preparation of specimens, and for highly intelligent use of equipment of maximum resolving

[107] Breed, N. Y. State Agr. Expt. Sta., Tech. Bul. 120.

[108] Dahlberg, N. Y. Agr. Expt. Sta., Tech. Bull. 111, 3 (1925).

[109] *J. Biol. Chem.*, **63**, lxvi (1925).

[110] *Ind. Eng. Chem.*, **18**, 190 (1926).

[111] *Am. Food J.*, **20**, 250 (1925).

[112] *J. Am. Chem. Soc.*, **47**, 2063 (1925).

[113] *J. Am. Pharm. Assoc.*, **14**, 873 (1925).

[114] Liddell, Handbook of Non-Ferrous Metallurgy, 6 (1926); *Trans. Am. Inst. Mining Met. Eng.*, **73**, 1135 (1926).

[115] *Gen. Elec. Rev.*, **28**, 573, 800 (1925); **30**, 160, 264 (1927).

[116] Metallography and Heat Treatment of Iron and Steel, 3rd ed., 1926.

[117] *J. Roy. Micros. Soc.*, **1925**, 393; *J. Franklin Inst.*, **201**, 177 (1926); *Iron Age*, **117**, 555 (1926).

power. Among the various new methods may be mentioned Guthrie's use of paraffin-coated polishing disks charged with abrasive,[118] and the microtome surfacing of the softer alloys by Lucas.[119] Jewell [120] has devised a new type of vertical illuminator to minimize the "glare" which is such a serious hindrance in the photomicrography of opaque objects. The etching characteristics of the various phases occurring in Al alloys are fully treated in a paper by Dix and Keith.[121] Green's article on eutectic patterns in alloys [122] illustrates a variety of typical forms and helps to unify our knowledge of these structures.

Zinc coatings have been studied microscopically by Finkeldey.[123] Kohlman and Sanborn [124] have investigated the iron-tin alloy in tin plate in connection with failures in cans.

The microscope is continually being used to follow the progress of the corrosion of metals and to recognize influencing factors such as segregations, strains, grain character and the formation of surface coatings. Christie [125] gives a review of the work on the embrittlement of boiler plate from 1866-1927, and Parr and Staub [126] show how local stress accelerates chemical attack and separation of salts may have a protective action where sulfates are in excess of carbonates and hydroxides in the boiler water. Chappell [127] uses the microscope to measure the thickness of rust films, and concludes that if the rust film is thick enough the rates of corrosion of different steels may be similar.

Rawdon's comprehensive paper [128] on the intercrystalline corrosion of metals points out that there is usually some structural condition to which the attack at the grain boundaries of the metal may be ascribed.

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[118] *Trans. Am. Soc. Steel Treating*, **7**, 337 (1925).
[119] *Am. Inst. Mining Met. Eng.*, **1654-E** (1927).
[120] *J. Optical Soc. Am.*, **14**, 159 (1927).
[121] *Proc. Am. Soc. Testing Materials*, **26**, II, 317 (1926).
[122] *Trans. Am. Inst. Mining Met. Eng.*, **71**, 651 (1925).
[123] *Proc. Am. Soc. Testing Materials*, **26**, II, 304 (1926).
[124] *Ind. Eng. Chem.*, **19**, 514 (1927).
[125] *J. Am. Waterworks Assoc.*, **17**, 174 (1927).
[126] *Ind. Eng. Chem.*, **19**, 620 (1927).
[127] *Ind. Eng. Chem.*, **19**, 464 (1927).
[128] *Ind. Eng. Chem.*, **19**, 613 (1927).

Chapter XVIII.

Aluminum.

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Production. The past year has seen further activity in the development of methods for the production of pure alumina to be used for electrolytic reduction to aluminum. Pedersen,[1] working in coöperation with the research staff of Aluminum Company of America, has further developed his process of producing alumina. The process involves treating bauxite or other ferruginous aluminous materials in an electric furnace with limestone and coke. A very pure iron is produced, together with a calcium aluminate slag. Pedersen now proposes to leach the calcium aluminate slag in sodium carbonate solution containing a small amount of sodium hydroxide in order to produce alumina substantially free from silica.

There has been considerable interest in the production of aluminates, such as calcium aluminate, which is the basic constituent of the high alumina cements. Hansen, Dyckerhoff, Ashton and Bogue [2] describe experiments carried out at the Bureau of Standards on the system, lime-alumina-silica. They state that the previously reported compound, $8CaO \cdot Al_2O_3 \cdot 2SiO_2$ is really a mixture of $3CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$ and $2CaO \cdot SiO_2$. Eckel [3] has described a modified process for producing aluminous cements and ferrosilicon in a blast furnace or an electric furnace. Myers [4] plans to heat alunite and limestone with a carbonaceous material in order to volatize the potash from the calcium aluminate cement formed in the reaction. Bates [5] has reviewed the characteristics of the high alumina cements from both the scientific and practical viewpoints. Barnitt[6] has developed the commercial production of sodium aluminate by heating ground bauxite, sodium carbonate and fuel on a sintering machine. McBride[7] has described the new aluminum reduction plant at Arvida, Canada, which promises to be the largest in the world when developed acording to present plans.

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[1] U. S. P. 1,618,105, February 15, 1927.
[2] *J. Phys. Chem.*, 31, 607 (1927).
[3] U. S. P. 1,591,662, July 6, 1926.
[4] U. S. P. 1,613,238, January 4, 1927.
[5] *Ind. Eng. Chem.*, 18, 554 (1926).

Alloys. The production of electrolytically refined aluminum having a purity of 99.95% or over has provided means of studying the properties of aluminum alloy systems without hindrance from the unavoidable impurities present in ordinary aluminum. Dix and his co-workers have previously determined the solubility limits of copper in aluminum and have also investigated the system aluminum-iron at the aluminum end of the diagram. Continuing this work, Dix and Keith[8] found that manganese was soluble in aluminum to the extent of 0.65% at the eutectic temperature, 657°C, and the solubility was less than 0.14% at 200°C. An unusual phenomenon was observed in the fact that manganese in excess of the solubility limit at the eutectic temperature could be present in so finely dispersed form as to be invisible under the highest possible magnification.

Dix and Keith[9] investigated the etching characteristics of the constituents in commercial aluminum alloys. They found that silicon, $CuAl_2$, Mg_2Si and Mg_2Al_3 are easily identified in polished sections without etching. $MnAl_3$, $NiAl_3$ and the iron compounds usually require etching for identification. Ternary compounds are also found in these alloys, as well as solid solutions of constituents in each other. They have tabulated a series of etching reagents, and the effect of these reagents on 13 different constituents which commonly occur in aluminum base alloys. A method is outlined by which the identification of these constituents becomes possible.

Archer[10] has made a critical study of the phenomena involved in the hardening of metals by dispersed constituents precipitated from solid solutions, and particularly the hardening of the alloys of aluminum. He has discovered that aluminum-copper-magnesium alloys practically free from silicon, and hence free from Mg_2Si, age-harden at room temperature to about the same extent as does ordinary duralumin containing silicon. A detailed understanding of the process of solution and precipitation in solid metals is doing much to advance the development of new and industrially important aluminum base alloys.

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[6] U. S. P. 1,616,674, February 8, 1927.
[7] *Chem. Met. Eng.*, 33, 724 (1926); 34, 76 (1927).
[8] *Am. Inst. Min. Met. Eng.*, Preprint 1633-E (1927).
[9] *Proc. Am. Soc. Testing Materials*, 26, Pt. II, 317 (1926).
[10] *Am. Soc. Steel Treating*, Preprint No. 22 (1926).

Jares[11] studied the system aluminum-zinc by the thermal and dilatometric methods. He found that decomposition of the beta crystals (Al_2Zn_3) occurred at 252°C on cooling. This value was low on account of supercooling and the transition temperature was taken at 280°C where it appeared on heating. The systems aluminum-zinc-tin and aluminum-zinc-cadmium were also studied by the method of thermal analysis. A eutectic containing 1% aluminum, 8% zinc and 91% tin melts at 196°C in the first of these systems. In the aluminum-zinc-cadmium system it was found that many of the alloys separate into phases of widely different density. The eutectic melts at 270°C and contains 0.3% aluminum, 25.7% zinc and 74% cadmium.

Daniels[12] investigated the properties of some sand-cast aluminum alloys containing cobalt, and found no useful alloy in the binary series containing up to 10% cobalt. The addition of more than 0.5% of this element increases the solidification shrinkage greatly and more than 1% imparts a crystalline structure whose coarseness is the more pronounced as the pouring temperature increases. Metallographic examination indicates a eutectic point in the neighborhood of 0.6% cobalt and it is doubtful whether the transformation line established by Gwyer has any proper basis. Daniels[13] has investigated the effect of low temperature heating on aluminum-copper-nickel-manganese and aluminum-copper-iron-manganese alloys such as are used in the production of pistons. Both alloys greatly soften on reheating and this softening is accompanied metallographically by the appearance of intergranular precipitate. Daniels[14] has also published the results of other experiments to determine the best heat treating conditions for aluminum alloys.

Pacz, who is largely responsible for the present interest in aluminum-silicon alloys, has described[15] a series of aluminum-silicon alloys containing about 3 to 15% silicon, together with other alloying elements such as manganese, cobalt, and copper and manganese. Pacz has also patented[16] another method for modifying aluminum-silicon alloys which depends upon treatment of the molten alloy with sodium hydroxide; this method apparently depends upon the reduction of sodium hydroxide to metallic sodium by the molten aluminum. Edwards, Frary and Churchill had previously used metallic sodium itself for the "modification" of aluminum-silicon alloys.

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[11] *Am. Inst. Min. Met. Eng.*, Preprint 1588-E (1926).

[12] *Ind. Eng. Chem.*, **18**, 686 (1926).

[13] *Am. Inst. Min. Met. Eng.*, Preprint 1519-E (1926).

[14] *Ind. Eng. Chem.*, **18**, 1280 (1926); *Trans. Am. Soc. Steel Treating*, **10**, 872 (1926).

[15] U. S. P. 1,595,218, August 10, 1926; 1,595,219, August 10, 1926; 1,595,058, August 3, 1926.

Additional details of the production of aluminum alloys by the electro-thermal reduction of alumina have been disclosed in a patent to Frary.[17]

The heat treatment of wrought aluminum-copper alloys, first discovered by Wilm, has been scientifically and technically developed to a surprising degree. It remained for Archer and Jeffries[18] to discover and develop the technique of heat treating aluminum alloy castings. An extensive commercial use is now being made of their process. Using electrolytically refined aluminum (99.95% pure) alloyed with 4.5% copper, they prepared a heat treated sand-cast test bar having a tensile strength of 54,000 lbs. per square inch and an elongation of 15%; these are probably the highest values ever obtained in sand castings of aluminum alloy.

Edwards and Taylor[19] measured the electrical resistivity of a series of aluminum-calcium alloys containing up to 3% calcium. The addition of 3% calcium increased the resistivity of rolled aluminum from about 2.70 to 3.30 microhms per cm^3. A higher resistivity was noted in the cast than in the rolled alloys, resulting from the special structural distribution of the aluminum-calcium constituent.

Miscellaneous. There have been a wide variety of values reported for the potential of aluminum in aqueous solutions. Kahlenberg and French[20] found that the potential of electrolytically refined aluminum in aqueous solutions of KCl was slightly higher than that of ordinary commercial aluminum. Oxygen depresses the voltage, which can be raised again by displacing the oxygen by nitrogen, hydrogen, illuminating gas, or carbon dioxide. The voltage can thus alternately be raised or lowered at will, showing that an oxide film is not the cause of the low voltage in oxygen, but that the low values are caused by oxygen adsorbed on the surface of the metal.

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[16] U. S. P. 1,596,020, August 17, 1926.

[17] U. S. P. 1,594,362, August 3, 1926.

[18] *Am. Inst. Min. Met. Eng.*, Preprint 1590-E (1926); Jeffries and Archer, U. S. P. 1,572,487, 1,572,488, February 9, 1926.

[19] *Trans. Am. Electrochem. Soc.*, 50, Preprint (1926).

[20] *Trans. Am. Electrochem. Soc.*, 50, Preprint (1926).

Something of a controversy has arisen over the discovery that Oersted undoubtedly anticipated Wöhler in the preparation of metallic aluminum. Tosterud and Edwards,[21] among others, have repeated Oersted's experiments and found that relatively pure aluminum can readily be prepared by the action of potassium amalgam on aluminum chloride.

Buffington and Latimer [22] used an interference method in measuring the thermal expansivity of aluminum at temperatures of 85 to 315°K. The expansion coefficient (α) at the lower temperature was 0.881×10^{-5} and 2.319×10^{-5} at the higher temperature.

Pacz [23] has developed a method of giving aluminum articles a mottled light and dark coating by a solution containing a fluosilicate, an alkali salt and a nickel or cobalt salt. The coloring can be controlled by varying the concentration of the solution or by alloying the aluminum with silicon, copper, zinc, etc.

Krase, Thompson and Yee [24] have reviewed the history of the aluminum nitride process, principally from the standpoint of the patent literature, together with the chemistry of the process. Nitrification experiments on the ferro-aluminum alloy showed that practically all aluminum in the alloy could be nitrified if such substances as cryolite, magnesium, aluminum, calcium fluoride or chloride were added to the pulverized alloy before nitrification.

Dunlap [25] has investigated coatings for protecting wood from moisture and noted the high efficiency for this purpose of paints made with metallic aluminum bronze powder in varnish vehicle.

Jones [26] recommends the plating of aluminum with cadmium in order to make it resistant to corrosion, especially salt atmosphere corrosion.

The American Society for Testing Materials revised their Tentative Methods of Chemical Analysis of Aluminum and Light Aluminum Alloys during the year.[27] These methods represent the most advanced as well as the most thoroughly tested methods available for the analysis of aluminum and are an important contribution.

[21] *Trans. Am. Electrochem. Soc.*, **50**, Preprint (1927).
[22] *J. Am. Chem. Soc.*, **48**, 2305 (1926).
[23] U. S. P. 1,614,684, January 18, 1927.
[24] *Ind. Eng. Chem.*, **18**, 1287 (1926).
[25] *Ind. Eng. Chem.*, **18**, 1230 (1926).
[26] U. S. P. 1,594,061, July 27, 1926.
[27] A. S. T. M. Specification Serial No. B40-261 (1926).

Although aluminum base alloys are very much more resistant to corrosion than steel, for certain kinds of structural work it seems that they are not as highly corrosion-resistant as desirable. The Bureau of Standards[28] has experimented with the protection of duralumin by various finishes and has found that a coating of pure aluminum applied by the "metal spraying" process is effective.

Dix has developed a new strong alloy product which has high resistance to the corrosion conditions usually met with in service.[29] This material, which he calls "Alclad," consists of a strong alloy core provided with a surface layer of pure aluminum, thus giving the useful combination of strength in the body of the alloy with high corrosion resistance at the exposed surface. The surface layer of pure aluminum is alloyed and integral with the strong alloy core and is very uniform in thickness. Dix has found that Alclad is resistant to corrosion even on cut edges or where the coating may have been cut through or damaged. This is apparently due to the fact that the pure aluminum surface is electronegative to the alloy and has the higher solution potential in any electrolytic action. Electrolytically refined aluminum with its exceptional resistance to corrosion can be used for the surface layer.

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[28] *J. Frank. Inst.*, 204, 113 (1927).

[29] Presented at Annual Meeting, National Advisory Committee for Aeronautics, May, 1927. To be published by the Committee as a Technical Note.

Chapter XIX.

Chromium Group Metals.

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During the period July 1, 1926 to July 1, 1927 chromium again, of all metals, played the most conspicuous and important part in chemical engineering. The main outstanding, characteristic properties of the metal and its alloys—resistance to corrosion at low and high temperatures, resistance to the attack of sulfur and many strong reagents, resistance to extreme wear, the high and enduring reflectivity of bright chromium metal surfaces, the long lasting, keen-cutting edges of chromium alloy tools—ensure an ever increasingly broad field of application in the arts and industries.

About 45% of the total production of chromium goes into the manufacture of alloys, about 35% into refractories and the balance, about 20%, into chemical compounds such as bichromates, chrome alums, etc.[1]

Physical and Chemical Studies. Wilson,[2] in his review of tanning during the period 1876-1926, emphasizes that during this period an entirely new method of tanning has come to the fore in which the tanning agent is basic chromium sulfate. The chromium salts penetrate the skins much more quickly than do the vegetable tannins and the combination of chromium and tannin is extremely stable. The development of chromium tanning was almost entirely dependent upon a knowledge of chemistry. In practice today the pH value, the temperature and the concentration of chromium in solution are carefully controlled. The process has proved of enormous value because it has greatly shortened the time of tanning and the risks involved.

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[1] Fink, *J. Soc. Auto. Eng.*, 20, 157 (1927); *Brass World*, 23, 159 (May, 1927).
[2] *Ind. Eng. Chem.*, 18, 934 (1926).

The effect of hydrogen ion concentration on the viscosity of hydrosols of chromic oxide was investigated by Yoe and Freyer[3] at the University of Virginia. The viscosities were measured at 25°C over a range of pH of about 2.5 to 9 and with sols containing 0.06, 0.03 and 0.015% of chromic oxide. The sols showed little or no change in viscosity with decreasing hydrogen ion concentration until a critical concentration of about $pH = 7$ was reached. At this point the viscosity increased rapidly to a maximum and then dropped fairly rapidly to an approximately constant value. It is possible that this change in the viscosity of the oxide hydrosol is due in part at least to a change in the degree of "hydration" using the term hydration in its most general sense. The water may be partly in true chemical combination; partly adsorbed on the surface and in the capillaries and partly occluded in the voids when the particles agglomerate into loose aggregates.

Riegel and Reinhard[4] studied the zone pattern formed by *silver chromate* in solid gelatine. The pattern proved to be similar to the one formed by copper ferrocyanide. The silver dichromate pattern is free from lines. As regards the color of silver chromate it has been assumed ever since the publication by Hunt[5] in 1845 that silver chromate precipitated from a light actinized solution had a "much more beautiful color" than the chromate precipitated from solutions not exposed to light. Now, however, Florence Bush,[6] at Cornell, finds that light does not affect the color. On the other hand she has established that the rate at which the precipitating solution is added to the bichromate solution determines the shade and other physical characteristics of the silver chromate formed.

Henderson and Kracek[7] found that the fractional precipitation of barium-radium chromate affords a means of separating the two elements which is comparable in effectiveness to the results obtained with the familiar bromide method. The partition factor D was found to be 15.5 for acid solutions. They recommend the chromate method for relatively small quantities of barium-radium mixtures and for the recovery of Ra from Ra-Ba solutions which are too lean to be economically concentrated by the chloride method.

[3] *J. Phys. Chem.*, **30**, 1389 (1926).
[4] *J. Phys. Chem.*, **31**, 713 (1927).
[5] *Mem. Chem. Soc.*, **2**, 311 (1845).
[6] *J. Phys. Chem.*, **31**, 931 (1927).
[7] *J. Am. Chem. Soc.*, **49**, 738 (1927).

Jenckes[8] described in detail the American manufacture of pure oxides and other salts of tungsten and molybdenum. Arsenic, an impurity in the original tungsten ore, is eliminated from the sodium tungstate solution by precipitation with copper sulfate. Phosphorus and silica remain in solution when the tungsten is precipitated as calcium tungstate. The addition of HCl to this precipitate produces insoluble WO_3 plus soluble $CaCl_2$. In the molybdenum leach solutions iron, as an impurity, is precipitated by hydrogen peroxide, copper as copper sulfide and calcium as calcium oxalate.

Engle[9] presented a detailed account of the gaseous reduction of tungsten and molybdenum oxides as carried out at the Chicago factory of the Fansteel Products Co. The reduction of WO_3 by hydrogen begins at about 620°C and that of MoO_3 at about 300°C. The difficulty in accurately determining small percentages of thorium in tungsten filaments is emphasized by Brophy and Van Brunt[10] of the General Electric Co.

Alloys. Tests on steel drums made of 17% Cr, 6% Ni steel were reported upon by the Manufacturing Chemists Association.[11] These drums resist nitric acid and certain concentrations of HCl and H_2SO_4. The drums successfully passed the I. C. C. 5-A tests. The Chrome Alloy Tube Corporation of New York started marketing stainless iron welded seam tubing containing up to 20 and 25% Cr.[12]

Grossmann[13] investigated the chromium-iron diagram. The system Fe-Cr is typical of iron alloy systems in which γ iron entirely disappears when sufficient alloying element is introduced and α iron becomes continuous. The amount of chromium to bring about this result is 14%. Another system showing similar behavior is Fe-W where γ iron disappears at 6% W.

Bain and Griffiths[14] of the Carbon and Carbide Research Laboratory showed that in the chrome-iron-nickel alloys there is a hitherto undescribed constituent found at temperatures between 800 and 950°C, having a hardness of 68.5 Rockwell. It is brittle, non-magnetic and possesses a complex crystal structure. Above 1000° only two kinds of solid solution appear to occur, *viz.,* austenite containing Cr and ferrite containing Ni. French[15] of the Bureau of Standards published a detailed report on Metals to Resist Corrosion or High Temperatures and points out the many advantages of chromium alloys. The welding of high chromium alloys is discussed by Norwood[16] of the Carbon and Carbide Research Laboratory. The important part played by chromium alloys in the construction of nitrogen fixation apparatus is pointed out by Thompson[17] on the basis of very exhaustive tests on various metals. Detailed reviews of the advantages of chromium alloys in chemical plant equipment were published by MacQuigg[18] and by Nelson.[19]

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[8] *Trans. Am. Electrochem. Soc.,* **51**, Preprint (1927).
[9] *Trans. Am. Electrochem. Soc.,* **51**, Preprint (1927).
[10] *Ind. Eng. Chem.,* **19**, 107 (1927).
[11] *Chem. Met. Eng.,* **34**, 355 (1927).
[12] *Chem. Met. Eng.,* **34**, 382 (1927).
[13] *Am. Inst. Mining Met. Eng.,* Preprint 1612-C (1926).
[14] *Am. Inst. Mining Met. Eng.,* Preprint 1850-C (1927).

Chromium Plating. The chromium plating industry has continued to grow in leaps and bounds. Millions of articles have been plated: Marine fittings, oil stills which show remarkable resistance to the corrosive action of sulfur compounds, plumbing fixtures which are unaffected by uric acid, chromium plated cobalt chrome mirrors, high temperature furnace parts, rubber molds, etc. Chromium plating plants have been established in every important centre of the country.[20]

[15] *Trans. Am. Electrochem. Soc.*, 50, 47 (1926).

[16] *Trans. Am. Electrochem. Soc.*, 50, 91 (1926).

[17] *Trans. Am. Electrochem. Soc.*, 50, 101 (1926).

[18] *Chem. Met. Eng.*, 33, 609 (1926).

[19] *Chem. Met. Eng.*, 33, 612 (1926).

[20] Phillips, *Brass World*, 23, 119 (1927); Proctor, *ibid.*, 23, 193 (1927); *Chem. Met. Eng.*, 33, 506 (1926); *ibid.*, 33, 434 (1926); *Metal Ind.* (N. Y.), 24, 332, 349 (1927).

Chapter XX.

Copper.

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Refining. There have been no important changes during the past year in the practice of refining copper. During the preceding year one of the marked advances in electrolytic refining was the control of the resistance of the electrolyte. The acidity was increased from 150 grams per liter to 200 or 220 g. per liter, resulting in a marked saving of power in the tank house. Recently several important papers have been published describing work that led up to this development. Skowronski and Reinoso [1] have found that within the limits of the composition of electrolyte used in copper refining the effect of copper, nickel, arsenic, and iron on increasing the specific resistivity of the electrolyte is directly proportional to the amounts added. Formulae have been derived for each of these metals, by the use of which the resistivity of an electrolyte may be calculated from its analysis. Rouse and Aubel [2] have shown that there is a decided drop in the total cell voltage with rise in temperature and with increase in acid concentration. On the other hand, an increase in $CuSO_4$ or in $NiSO_4$ or in As_2O_5 concentration has but a slight effect on the total cell voltage within operating range. Fink and Phillippi [3] have studied the anode and cathode polarization and internal resistance drop through the copper electrolyte under varying conditions. Their results indicated the importance of studying and controlling the voltage at both cathode and anode surfaces in order to arrive at the most efficient refining operating conditions.

Technology. Smith and Hayward [4] have studied the penetration of copper by hydrogen at various temperatures. They have found that when brittle gassed copper is annealed and forged in a non-oxidizing atmosphere, the cracks responsible for the brittleness close, and a metal of remarkable properties is obtained. The superiority in certain respects of phosphorized over tough pitch copper for the manufacture of small sizes of seamless copper tube was pointed out by Webster, Christie, and Pratt.[5] Zickrick and Dean[6] have shown that the annealing temperature of hard-drawn copper wire depends to a marked degree on its previous treatment as regards cold working and annealing. Bradley[7] presented figures showing the relation of annealing temperature to conductivity of copper wire, supplementing results of previous investigation.

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[1] *Trans. Am. Electrochem. Soc.*, **51**, Preprint (1927).
[2] *Trans. Am. Electrochem. Soc.*, **51**, Preprint (1927).
[3] *Trans. Am. Electrochem. Soc.*, **50**, Preprint (1926).
[4] *J. Inst. Metals*, **36**, 211 (1927).

Cooperative investigation to establish the effect of impurities upon the physical properties of refinery copper is being carried out by a producer and a consumer. This is a monumental work and will require a few years for completion. Work in this field is also being carried out at an Eastern University.

Alloys. The duralumin reaction has been applied by Corson[8] to copper. The compounds Ni_2Si, Co_2Si, and Cr_2Si form alloys with copper, their solubility being very low at room temperature, but amounting to several % at 1000°C. On reheating at 350 and 550°C, the compounds are precipitated in ultramicroscopical form, giving increased hardness, strength and electrical conductivity. Nickel silicide shows the greatest effect. The fundamental atomic conditions existing in Corson's high-copper alloys have been investigated by Bain.[9] Bassett[10] has noted that combinations of manganese with silicon can also be similarly employed but with less effect than nickel silicide. The properties of copper-silicon alloys have been described by Corson.[11]

The alloy of copper with silicon up to about 3% with the addition of manganese has been patented by Jacobs and is being marketed under the name of "Everdur." While this alloy is comparatively new it is a plain solid solution and promises well as an engineering material for severe service, on account of its physical properties and resistance to corrosion.

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[5] *Trans. Am. Inst. Min. Met. Eng.*, Preprint No. 1643-E (1927).
[6] *Trans. Am. Inst. Min. Met. Eng.*, Preprint (1927).
[7] *Trans. Am. Inst. Min. Met. Eng.*, Preprint No. 1646-E (1927).
[8] *Iron Age*, 119, 421 (1927).
[9] *Trans. Am. Inst. Min. Met.*, Preprint No. 1657-E (1927).
[10] *Min. Met.*, 8, 214 (1927).
[11] *Iron Age*, 119, 353 (1927).

In the field of copper-zinc alloys Miss Clark[12] has made an interesting study of the heat-treatment, microstructure, and hardness of 60-40 brass.

Results of investigation of copper-beryllium alloys were presented by Bassett[13] with tables showing their physical properties as compared with those of other high copper alloys. The metallographic aspects of the beryllium alloys were described in a paper by Corson.[14] It seems probable that, with beryllium at commercial prices, its alloys might be used for springs, stronger wires, and high-strength conductors.

A group of alloys of considerable present interest is that used for high-strength conductors. Cadmium is the best of the commercially available materials for alloying with copper where the least possible reduction in conductivity is required. The maximum alloy which at present can be hot rolled contains 1.25% cadmium. Higher strength than can be had with cadmium alone may be obtained with a combination of cadmium and tin, with less reduction of conductivity than must be accepted when tin alone is used.

Probably the best of the corrosion-resistant alloys are the copper-nickels. Although they have been known to industry for a long time, they have not been understood and hence have been very hard to handle. Recently the realization of the fact that these alloys were strong, particularly resistant to corrosion, of excellent appearance, and not subject to stress failures has brought them into deserved popularity. The copper-nickel alloys with low-zinc are particularly suitable to engineering and architectural requirements. A recent development in this type of alloy has been to increase the nickel content to some 30%, resulting in improved physical properties.

Corrosion. The importance of the study of corrosion problems is definitely established, and considerable work is being done in this field by industries, schools, and technical societies.

A study by Russell and White[15] has shown that the corrosion of copper by dilute acids was directly proportional to the amount of dissolved oxygen present.

An impetus was given to the constructive development of alloys and, in particular, corrosion-resistant alloys by Guertler in a series of admirable lectures during a tour of this country in 1926. The substance of one of his lectures on corrosion-resistant alloys has been published recently.[16]

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[12] *Trans. Am. Inst. Min. Met.*, Preprint No. 1630-E, 1637-E (1927).
[13] *Trans. Am. Inst. Min. Met.*, Preprint No. 1634-E (1927).
[14] *Brass World*, 22, 314 (1926).
[15] *Ind. Eng. Chem.*, 19, 116 (1927).

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[16] *Z. Metallkunde,* **18**, 365 (1927).

Chapter XXI.

Iron and Steel.

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Direct Reduction of Iron Ore. Davis[1] describes the making of iron without coke, using a retort which resembles a coke oven. The ore in contact with coal is reduced to sponge iron in the upper part of the furnace and discharged to the lower portion for cooling, out of contact with the air. He also discusses the general process for making iron directly from the ore and subsequently melting the sponge iron briquets in an oil fired open hearth furnace of 3 tons capacity.

Coke Manufacture. An apparatus has been installed at the West Station at the Rochester Gas and Electric Corp.,[2] for the dry quenching of by-product coke by the circulation of so-called "inert gases" through a large mass of coke in varying stages of quenching. The plan is patterned after the design adopted by the Sulzer Frères of Winterthür, Switzerland. The entering coke has a temperature of 1800°F., while on leaving the quencher it is at about 350°F.

The Blast Furnace. Ross[3] describes the blowing in of a repaired blast furnace with oxygen.

A study of the reactions in an iron blast furnace by Kinney, Royster and Joseph,[4] describes the results of the investigation of this subject by metallurgists of the U. S. Bureau of Mines as part of a general investigation of the combustion of coke and the reduction of iron oxides in a blast furnace.

Imhoff[5] sums up the principles governing the interpretation of blast furnace slags. He gives fifteen principles which govern their interpretation and shows reasons for "off" iron and how it can be corrected.

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[1] *Iron Trade Rev.*, **80**, 133, 197 (1927).
[2] Koon, *Iron Age*, **119**, 425 (1927).
[3] *Mining and Met.*, **7**, 253 (1926).
[4] *Iron Age*, 118, 165 (1926). Bureau of Mines, Repts. of Investigations, No. 2747.
[5] *Iron Age*, **118**, 612 (1926).

The Foundry. The problem of obtaining and testing the proper kinds of sand for foundry molds has been one of the chief subjects of discussion before the American Foundrymen's Association.[6] At the fall convention of the American Foundrymen's Association were many papers on the methods of testing sand and sand control for the foundry. The important papers were as follows: Ries reported progress in ascertaining and recommending the best tests for various properties of sand. Saunders reported that the Committee on Molding Sand Research has already collected and tested over 1100 samples of molding sands. He suggests the study of clay substance in sands. Harrington reported for the Sub-committee on Conservation and Reclamation that 35 different clays have been studied and tested and considerable progress has been made on the subject of sand reclamation. Grubb stated that the Sub-committee on Grading has studied 727 sets of test data from all parts of the country.

The Manganese Problem in the Steel Industry. At a special session of the Ohio Section,[7] American Institute of Mining and Metallurgical Engineers, in Cleveland on April 19, the subject of manganese was thoroughly discussed. Leith opened with an address on the political aspects of the world manganese situation. He called attention to the fact that nearly 85% of the world's production of manganese is used by the United States, England, Germany and France and that the United States consumes roughly one third of the total. On the other hand, over 85% of the world's production comes from Brazil, Russia, India, the Gold Coast of Africa and the Sinai peninsula. He pointed out also that the steel industry uses over 90% of the manganese used, and indicated four possible solutions of the manganese problem in the North Atlantic countries: Development of domestic supplies; substitutions for manganese; storage; and control of channels of flow from the sources. Boylston pointed out the importance of manganese in the steel industry and showed that the United States requires annually about 450,000 gross tons of 80% ferromanganese or its equivalent. Corson dealt with the subject of manganese in non-ferrous alloys. Herty, Jr.,[8] calls attention to the fact that nearly 280,000 tons of manganese were wasted in 1926 in open hearth slags. He calculates these losses and advocates the recovery of manganese from slags by charging them into the blast furnace or by utilizing them as raw material in the manufacture of Spiegel or ferromanganese.

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[6] *Iron Age,* **118**, 1077 (1926).
[7] *Iron Age,* **119**, 1209 (1927).
[8] *Iron Age,* **119**, 1068 (1927).

Open Hearth Design and Practice. Fitch[9] calls attention to the use of recuperators for open hearth furnaces and describes the arrangement used in one large plant. The recuperator is built up of tubes of silicon carbide which are treated to prevent them from oxidizing. Herty, Jr.,[10] has studied carefully the basic open hearth process and gives data and graphs showing the rapidity and completeness of elimination of the metalloids in an open hearth heat. He also gives graphs showing the change in slag composition during the same heats.

Herty, Jr.,[11] also discusses the three types of charges in basic open hearth practice; the first two are pig iron and scrap heats with no ore in the charge, the first being charged with very large scrap, the second with medium scrap; the third heat is an iron ore heat, 20,000 lbs. of ore being charged with the scrap. The effect of sulfur in the gas on the sulfur content of the metal is discussed and illustrated. Lowry[12] discusses slags, fluxes and desulfurizers used in the basic open hearth process. He points out the important effect of temperature and a number of experiments were made at open hearth plants using quite a wide variety of fluxes. Experimental results are listed with certain conclusions of the author. Diehl[13] discusses the action of sulfur in basic open hearth practice. He concludes that the most assured method of producing low sulfur basic open hearth steel is to use materials containing a minimum quantity of that element. He points out that while gas free from sulfur is preferable, by-product or producer gas will give satisfactory results if the gas be burned so as to oxidize the hydrogen sulfide before coming in contact with the metal or scrap. Slag conditions are of primary importance and the slag should be oxidizing and basic and sufficiently fluid to effect the proper interchange between metallic and non-metallic baths.

The use of high manganese pig iron and manganiferous ores in open hearth practice is discussed by Smith.[14] It is his opinion that the advantages of the use of manganiferous pig are greater than the disadvantages.

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[9] *Iron Age,* **119**, 920 (1927); *Eng. Soc. W. Pa.,* **42**, 506 (1927).
[10] *Iron Age,* **118**, 610 (1926).
[11] *Trans. Am. Soc. Steel Treating,* **11**, 569 (1927).
[12] *Trans. Am. Soc. Steel Treating,* **10**, 906 (1926).
[13] *Iron Age,* **118**, 1196 (1926).
[14] *Iron Age,* **118**, 1193 (1926).

Sperr, Jr.,[15] describes a gas purification process which is said to increase the output of open-hearth furnaces. The Seaboard process, as it is called, consists essentially in scrubbing coke oven gas with a dilute solution of sodium carbonate. By this means 85 to 95% of the hydrogen sulfide and hydrocyanic acid is removed. The solution is subsequently revivified by aeration.

Ingots and Ingot Making. A study of the solidification of steel in the ingot mold is reported by Feild.[16]

Hibbard[17] discusses factors to be considered in controlling segregation in steel.

Alloy Steels and Iron Base Alloys. Sykes[18] describes the carbon free alloys of iron and molybdenum and includes the equilibrium diagram of this system as determined from fusion temperatures, heat treatments and a study of the accompanying microstructures. He finds a eutectic at 36% molybdenum melting at 2625°F. (1440°C.), a glass-hard inter-metallic compound Fe_3Mo_2 at 53.4% molybdenum, and appreciable solid solubility increasing with rise in temperature at either end of the system. The temperature solubility relations make possible the development of a secondary hardness by aging a supersaturated solid solution at 1112 to 1292°F. (600 to 700°C.). This hardness is equal to that of high speed steel and persists at temperatures considerably higher. He finds that the Ar_3 point is raised to 1795°F. (980°C.) by the addition of 3% of molybdenum to pure iron. With a molybdenum content greater than 3.5 or 4% the iron exists in the body-centered crystal lattice at all temperatures below the melting point.

The results of some tests on a new low carbon, high silicon structural steel known as "F" or Freund steel is reported by Gillett[19] of the U. S. Bureau of Standards. It is said that the steel contains 1% silicon and 0.15% carbon, this combination giving a high yield point and ductility.

Making rustless iron (carbon less than 0.1%, Cr between 11 and 16%) is described by du Bose.[20] The iron is made in an electric melting furnace. The charge is scrap steel or iron melted to a bath of molten metal containing less than 0.05% carbon and covered with a natural or prepared slag which will insure reasonably low sulfur and phosphorus content. A mixture of ferro silicon and good quality chrome ore with lime and other fluxes is added and the steel deoxidized and poured.

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[15] *Iron Trade Rev.,* **79,** 1046, 1358 (1926).
[16] *Trans. Am. Soc. Steel Treating,* **11,** 264 (1927).
[17] *Iron Age,* **118,** 1546 (1926).
[18] *Trans. Am. Soc. Steel Treating,* **10,** 839 (1926).
[19] *Iron Age,* **118,** 481 (1926).
[20] *Iron Trade Rev.,* **80,** 457 (1927).

McVetty and Mochel[21] describe the tensile properties of stainless iron and other alloys at elevated temperatures. Charts are presented to show that a comparison of the normal temperature tensile properties of materials does not indicate their relative value at elevated working temperatures. The tensile properties of annealed stainless iron and hot rolled Monel metal at temperatures up to 500°C., (930°F.) are discussed and compared with similar properties of seven other materials.

Stainless iron is also discussed by Mochel.[22] Data are given as to the physical properties of low carbon chromium iron alloys known commercially as "stainless iron." The alloys tested varied in composition and in heat treatment. Special attention was given to elastic limit and impact values. The effect of varying chromium content, and of silicon, copper and nickel on the physical properties, microstructure, resistance to corrosion and workability of the alloys is discussed.

The behavior of carbon in a high chromium rustless iron is discussed by Grossmann.[23] The carbon in a high chromium iron was found to be distributed non-uniformly after heat treatment. Separate austenite areas were found in equilibrium with regions of alpha iron. The metal is still soft after rapid quenching from a high temperature because most of it has remained as alpha iron, but the ductility of the metal is decreased greatly because of the formation of well distributed austenite areas, and these upon quenching become martensitic (and therefore hard) and so interfere with deformation.

The Development of Chromium Plating. Phillips[24] describes the present development of chromium plating and its application to automobile manufacture. He points out that the cost is not excessive if the operation is properly carried out. He also points out that the method has been successfully used on gages. In the case of small spindles, over a million have been chromium plated in place of carburizing and case hardening.

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[21] *Trans. Am. Soc. Steel Treating,* **11, 73 (1927).**

[22] *Trans. Am. Soc. Steel Treating,* **10, 353 (1926).**

[23] *Trans. Am. Soc. Steel Treating,* **10, 436 (1926).**

[24] *Iron Age,* **119, 773 (1927);** *J. Soc. Autom. Eng.,* **20, 255 (1927).**

Such spindles carry a very low load per square inch but are subject to extreme wear conditions. The chromium plated materials stood up better than when they were carburized.

Blum[25] discusses the commercial development of chromium plating and points out its application to steel gages. Some details of the process are given.

Metallographic Research. Schwartz and Johnson[26] have studied the graphitization of iron carbon alloys at constant temperature below the critical point. They find evidence that the mechanism of the reaction, in its earlier stages at least, is identical above and below the critical point. They show further that the apparent permanence of the metastable system at atmospheric temperatures is not inconsistent with the conception that graphitization proceeds at any temperature no matter how low.

Schwartz[27] gives evidences concerning the location of the carbon atom in boydenite, which is his name for the solid solution bearing the same relation to the stable alloys of iron and carbon which austenite bears to the metastable alloys. It is suggested that boydenite is a solution of carbon in gamma iron in which one atom of the former replaces one of the latter in the face-centered cubic arrangement.

Evans and Hayes[28] discuss the graphitizing behavior of iron carbide in pure iron-carbon alloys in the critical range. Experimental proof is presented that iron carbide in iron carbon alloys of rather high purity and containing about 2.30% carbon is metastable at temperatures below 1292° F., (700° C.) and at temperatures above 1562° F., (850° C.) in the presence of a mixture of carbon monoxide and carbon dioxide under a pressure of 5 atmospheres.

Dowdell and Harder[29] describe in considerable detail their study of the decomposition of the austenitic structure in steels. They discuss the decomposition of austenite during quenching; the decomposition of austenite in liquid oxygen; the effect of tempering temperature on the decomposition of austenite and the effect of stress on the decomposition of austenite.

Miscellaneous Research on Iron and Steel. Lessells[30] gives data on the tensile and fatigue properties of very hard steels, and shows the superiority of medium carbon steel in gear application. He discusses the relationship between the tensile strength, Brinell hardness and endurance limit and shows how residual stresses present in material may influence such a relationship.

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[25] *Iron Age.*, **118**, 1685 (1926).

[26] *Trans. Am. Soc. Steel Treating*, **10**, 965 (1926).

[27] *Trans. Am. Soc. Steel Treating*, **11**, 277 (1927).

[28] *Trans. Am. Soc. Steel Treating*, **11**, 691 (1927).

[29] *Trans. Am. Soc. Steel Treating*, **11**, 17, 217, 391, 583, 781 (1927).

[30] *Trans. Am. Soc. Steel Treating*, **11**, 413 (1927).

The corrosion-fatigue of metals as affected by chemical composition, heat treatment and cold working is discussed by McAdam, Jr.[31] The author is of the opinion that corrosion-fatigue depends on two factors: corrosion intensity and a stress range; and that the corrosion-fatigue limit depends on a strength factor as well as on corrosion-resistance. He discusses his experiments with carbon steels, nickel steels, high chromium steels and chromium-nickel steels and gives the effect of chemical composition and physical properties on corrosion-fatigue.

Embrittlement of boiler plate is discussed by Straub,[32] who outlines reasons for the formation of cracks and discusses the use of the microscope as an aid in determining the character of cracks. The causes for prevention are also discussed and it is his belief that the real causes of embrittlement in steam boilers is concentration of caustic soda in the seams in the absence of sufficient sulfate or carbonate together with the existence of localized stresses in the seams.

Lucas [33] publishes his observations on the microstructure of the path of fatigue failure in a specimen of Armco ingot iron. Nonmetallic inclusions appear to act as stepping stones for the crack. Inclusions seem to influence the origin and trend of the crack. Grain boundaries do not appear to be a potential source of weakness.

Bain and Grossmann [34] present some fundamental characteristics of the oil quenching type of tool steels. The data offered were obtained from measurements of hardness, impact strength, change of dimension and determination of X-ray crystal structure, as these properties are changed with various quenching and tempering temperatures. Deductions are drawn as to the preservation and subsequent destruction of austenite and this phenomenon is correlated with the practical behavior of the steel in its various uses.

The action of pure carbon monoxide upon iron at elevated temperatures is discussed by Fishel and Wooddell.[35] The conclusions drawn from this work are: That pure carbon monoxide reacts with iron at temperatures between 1470 and 2010°F. (800 and 1100°C.), to form iron carbide and carbon dioxide; that the reaction is reversible and obeys the laws of reversible reactions; that the depth of case increases with increase of temperature while the maximum carbon content in the case decreases. Total carbon introduced increases with increasing temperature; that both carbon monoxide and dioxide penetrate iron very slowly at 1740 and 2010°F. (950 and 1100°C.). This rate would not account for the depth of case produced by carbon monoxide.

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[31] *Trans. Am. Soc. Steel Treating,* **11**, 355 (1927).
[32] *Forging-Stamping-Heat Treating,* 13, 89 (1927).
[33] *Trans. Am. Soc. Steel Treating,* **11**, 531 (1927).
[34] *Trans. Am. Soc. Steel Treating,* 10, 883 (1926).
[35] *Trans. Am. Soc. Steel Treating,* **11**, 730 (1927).

Merten [36] discusses the wear resistance of carburized steel as compared with cast high manganese steel. He finds that plastic flow under heavy pressure during a gliding motion is apparently the cause of considerable abrasion on manganese steel of 14% manganese, while it has decidedly less influence upon case hardened steels.

Hillman and Clark [37] discuss cyanide brittleness and conclude that although water quenched steel parts, cyanided at 1500°F., are brittle, the brittleness in the core is apparent and not real.

The National Bureau of Standards [38] has discovered by tests that the resistance which steel offers to magnetization does not truly represent the magnetic properties of the material and therefore cannot be expected to serve as a basis for correlating them with mechanical properties of the metal.

Weber [39] presents results of studies on electric welding. He has studied the effect of various gases on metal deposited in electric welding as well as the effect of the arc on the gases. His experiments show that abnormal carburizing steels were produced when the steel was deposited in an atmosphere of carbon dioxide, carbon monoxide, nitrogen and air, while normal carburizing steel was produced when the weld was made in an atmosphere of helium. He finds that nitrogen combines with iron to form a nitride, part of which is retained in the deposited metal and part of which is condensed on the sides of the container. The analyses of the deposit suggest the formula Fe_5N_2.

Adams [40] has presented a comprehensive paper on the welding of iron and steel and concludes that the establishment of welding as a dependable industrial tool has opened up a new era as to

[36] *Trans. Am. Soc. Steel Treating,* 11, 233 (1927).
[37] *Trans. Am. Soc. Steel Treating,* 10, 954 (1926).
[38] *Iron Age,* 119, 1226 (1927); Bureau of Standards, Scientific Paper No. 546.
[39] *Trans. Am. Soc. Steel Treating,* 11, 425 (1927).
[40] *Iron Age,* 118, 1194 (1926).

economics and other gains which may be effected in fabrication. Among the most important factors are skilled workmanship, supervision, inspection, proper welding wire and base material, design, proper technique and suitable apparatus.

Weinman [41] has described processes of welding in the atomic hydrogen flame, developed by Langmuir and Alexander. In both processes air is excluded from the metal by means of a bath of hydrogen or other gas. It is claimed that the formation of oxides and nitrides is thus prevented, the fused metal being as strong and ductile as the original metal. The apparatus is still in the experimental stage.

Candy [42] has described the results of comparative tests on arc welded and riveted structural steel members. His tests are said to have proved conclusively that properly designed and fabricated arc welded connections have many merits.

St. John [43] describes mobile X-ray equipment for examining castings, welds and metals where located. Norton [44] describes the testing of welded joints by means of X-ray apparatus and concludes that radiographs will definitely show, in the case of welded joints, inclusions of gas, slag, oxide or other impurities whose thickness in a direction parallel to the X-ray beam is more than 5% of the total thickness of the sample; they will show the presence of cracks or seams which are nearly parallel to the direction of the X-ray beam but will not show cracks which are normal to it; the method will not tell anything about the crystalline condition of the metal; it will, however, indicate the failure of welding material to join completely the base metal plates.

The Jones and Laughlin Steel Corporation [45] has developed a new steel known as Jalcase which is adaptable for forging and case hardening and yet has the machinability of ordinary free cutting steels. The results of certain tests show that case hardened steering worms of Jalcase machined 23% faster than S.A.E. 1020 steel and showed a normal case free from soft spots and tested 60 Rockwell hardness (C Scale). It is claimed that the rate of carbon penetration is greater by 15 to 25% than in some grades of case hardening steel and that there is little distortion after heating and quenching. Other machine tests showed Jalcase steel to have better machining properties than S.A.E. 1020.

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[41] *Iron Age*, 117, 989 (1926); 118, 1485 (1926).
[42] *Iron Age*, 118, 344, 1485 (1926).
[43] *Iron Age*, 118, 783 (1926).
[44] *Iron Age*, 118, 409 (1926).
[45] *Iron Age*, 118, 546 (1926).

Jalcase is said to contain 0.12% sulfur, 0.12% carbon and 1.40% manganese.

Hayes and Wakefield[46] discuss the carbon content of pearlite in iron-carbon alloys containing one % silicon. They find a value of 0.669% carbon. Allison[47] describes spheroidization in steel and the method of its occurrence. He points out its relation to grain growth and grain boundaries and gives an explanation of Stead's brittleness. Krivobok[48] discusses dendritic crystallization and grain formation in steels. He maintains that dendritic segregation is not the sole cause of defective steel and that a pronounced dendritic structure is not sufficient cause for the rejection of steel. The heat of formation of cementite has been determined calorimetrically by Brodie, Jennings and Hayes.[49] They find a value of — 13,580 calories per gram molecule at 86° F.

Rawdon, Hidnert and Tucker[50] discuss some effects of hydrogen on iron and their bearing on a reported transformation at 698° F. By means of thermal analysis an "irregularity," appearing as an evolution of heat upon heating, the maximum being around 573° F., was detected in some iron specimens, the effect being more pronounced in specimens which had been heated in hydrogen. An irregularity in thermal expansion around 698° F. was likewise detected in some similarly treated specimens. Iron containing an appreciable amount of iron oxide showed this phenomenon best. Iron charged with "cathodic" hydrogen behaved irregularly in thermal analysis on heating, but showed an absorption of heat. The results of the investigation did not confirm the existence of the reported transformation.

Freeman, Jr.,[51] reports results obtained from the study of the recrystallization temperatures of cold rolled electrolytic iron and open hearth steel strip. This study is a continuation of a previous investigation of the comparative cold rolling characteristics of the two types of material. Tensile tests and microstructural studies were made. It was found that electrolytic iron underwent a marked recrystallization when annealed for one-half hour at 930° F., coincident with a pronounced decrease in tensile strength. Incipient recrystallization was noted in a specimen annealed for 24 hours at 750° F. In the open hearth steel a similar marked recrystallization was observed in specimens annealed for one-half hour at 930°F. The conclusion was reached that electrolytic iron would probably give somewhat superior material for deep drawing operations.

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[46] *Trans. Am. Soc. Steel Treating*, 10, 214 (1926).
[47] *Iron Age*, 118, 78 (1926).
[48] *Trans. Am. Soc. Steel Treating*, 10, 758 (1926).
[49] *Trans. Am. Soc. Steel Treating*, 10, 615 (1926).
[50] *Trans. Am. Soc. Steel Treating*, 10, 233 (1926).
[51] *Trans. Am. Soc. Steel Treating*, 10, 67 (1926).

The Bureau of Standards[52] has been studying the testing of metals at high temperatures under tension while subject to static stresses over long periods, and during the work, short time tests were developed for obtaining useful relations by which a rapid approximation of load carrying ability could be made. The work included the construction of a special extensometer by which it is possible to measure, at various temperatures, strain of the order of a few millionths of an inch.

List of Suggested Research Problems

The subjects listed on pages 29 and 30 of the Survey of American Chemistry, Vol. I, 1925-26 are still as live as ever and to them should be added the following:

1. Determination of the nature of the white hard constituents found in high speed steel and variously described as carbides and tungstides.
2. The nature of the constituent martensite.
3. The determination of the specific heat of molten steels and cast iron.
4. Substitutes for ferro-manganese in steel making.
5. Methods for the direct reduction of iron ore to metallic iron.

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[52] *Iron Trade Rev.*, 79, 319 (1926).

Chapter XXII.

Magnesium.

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Production. The steady progress made in the magnesium industry is revealed by the statistics of the Bureau of Mines, Department of Commerce. There was an increase of 30% in the tonnage sales of 1926 as compared to 1925. The sale of castings increased eleven-fold, and wire and tubing four-fold. These increased sales, coupled with process improvements, are rapidly lowering the price of the metal.

Foundry Practice. Current practice is divided as to the advisability of using fluxes in the founding of magnesium alloys. Most foreign investigators, however, now recommend the use of a flux to clean the metal and reduce losses, even though they do not entirely agree as to the most suitable composition and technique. Archbutt and Jenkins[1] use a flux composed of anhydrous $MgCl_2$ to which has been added small amounts of KCl, NaF and CaF_2. The flux has good covering power but is viscous enough to be held back by skimming. Dross losses were thus reduced to 5-6%. Cook and Jones[2] not only use a $MgCl_2$-MgF_2 flux but also advocate the "double melting" process and a bottom pouring crucible in order to minimize flaws. A more detailed description of this method and related technique is given by Jones.[3] Fleury[4] has shown that the protection of the molten metal by a salt bath with a fluoride base, or at least a puddling of the metal with such a bath between casting operations, is indispensable for the production of clean sound castings. Complete details of the method are given in the specifications of the Société de l'Electrochimie covering the melting, casting, and scrap recovery of magnesium alloys. Reiniger[5] states that the protection of molten magnesium by sulfur[6] was not complete and that the German foundries have also resorted to a chloride-fluoride-oxide flux. In general, it may be stated that improved foundry technique is yielding castings with superior properties and better corrosion resistance.

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[1] Brit. Aero. Res. Com. Rept. and Memo. No. 1037 (1926).
[2] *J. Inst. Met.*, 36, 157 (1926).
[3] *J. Roy. Aero. Soc.*, 30, 743 (1926).
[4] *Rev. de Met.*, 23, 649 (1926); *Met.* (Supp. to Eng.), Jan., 1927.

Corrosion. The corrosion of magnesium and its alloys is now receiving attention worthy of the problem. Unfortunately, the lack of suitable standardized methods for measuring the corrosion of this type of alloys is responsible for many contradictory statements. The more important recent contributions on this subject are those by Portevin and Boyer. Portevin[7] concludes that silicon is the most detrimental of the impurities present in magnesium. Some magnesium-base alloys show considerably more corrosion than magnesium, and in these cases the influence of the impurities becomes negligible. Boyer[8] has made a systematic study of the corrosion-inhibiting action of manganese on magnesium-aluminum alloys. Its beneficial action is thought to be due to the fact that it raises the overvoltage of the alloys back to that of pure magnesium. A critical amount of manganese is necessary, this amount increasing with the quantity of aluminum in solid solution. Non-metallic inclusions and magnesium silicide are claimed to be inactive.

Alloys. A wide variety of magnesium-base alloys is being investigated both in this country and abroad. The magnesium-copper alloys have been studied by Cook and Jones[2] in an effort to produce sound chill-cast bars. They give the effect of copper on physical properties and structure. The maximum tensile strength of approximately 21,000 pounds per square inch was obtained on the 2% alloy. Hanson[9] shows that magnesium is capable of holding about 0.5% copper in solid solution at 485°C. and 0.1% at room temperature. No age-hardening effect was obtained. A tensile strength of 31,000-47,000 pounds per square inch was secured on alloys containing 6-15% copper after being twice extruded. Archbutt and Jenkins[1] determined some of the mechanical properties of certain wrought magnesium alloys. Portevin and Le Chatelier[10] investigated the electrical resistance

[5] *Z. ges. Giesser.* **47**, 129, 133 (1926); *Chimie et Industrie,* **17**, 421 (1927).

[6] U. S. P. 1,540,867 (1925).

[7] *La Revue de l'Aluminum,* **2**, 161 (1926); *J. Inst. Met.,* **35**, 574 (1926).

[8] National Advisory Committee for Aeronautics, Report No. 248.

[9] *J. Inst. Met.,* advance copy No. 428 (1927).

[10] *Compt. Rend.,* **182**, 382 (1926).

and thermal expansion of many types of alloys. These data were studied, along with the mechanical properties, and the conclusion reached that the magnesium-nickel and magnesium-copper binary alloys, together with the magnesium-aluminum-nickel and magnesium-aluminum-copper ternary alloys, offer the best combinations of properties for certain applications such as pistons for motors. A complete résumé of the constitutional diagrams and mechanical properties of the magnesium-aluminum and magnesium-zinc alloys is given by Stoughton and Miyake.[11] They have also submitted a metallographic study of these systems and claim that up to 10 per cent zinc will form a solid solution with magnesium as evidenced by the hardening of these alloys.

Jones [3] has published a general review of magnesium-base alloys, which contains comparisons with other metals.

The most condensed résumé of properties is found in the International Critical Tables.[12]

Regelsberger [13] has supplied us with a valuable contribution on magnesium and its alloys, which covers all phases of the problem; namely, production, alloys and their properties, mechanical working, and economic factors. It has failed to make suitable mention of American progress, but is quite satisfactory from the European standpoint. The numerous patent references are especially valuable.

Uses. The interest in magnesium is now focused on airplane construction. Our country has lagged behind Europe in applying these alloys to this industry. The new impetus given to aeronautics, however, is already reacting favorably toward magnesium. Successful applications in this field cover various types of castings and wrought parts. Fleury [4] forcefully points out the economic advantages that are to be gained by substituting the ultra-light magnesium for the light aluminum alloys.

Zinc-base die casting alloys [14] have been improved by the addition of small amounts of magnesium. The use of magnesium in aluminum-base alloys [15] is likewise increasing, especially abroad.

The production of resonator discs for auto horns and talking machines continues to grow. A new use [16] for castings is in machine shop jigs.

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[11] *Trans. Am. Inst. Mining Met. Eng.*, 73, 541 (1926).

[12] *International Critical Tables*, 2, 544-545 and 604 (1927).

[13] *Chemische Technologie der Leichtmetalle und ihrer Legierungen*, Leipzig (1926).

[14] *Met. Ind.*, 25, 99 (1927).

[15] *Brass World*, 23, 76 (1927).

[16] *Met. Ind.* (London), 30, 39 (1927).

PROBLEMS.

Problems of the greatest practical importance today are those relating to the application of magnesium alloys to aircraft construction. They include:—

1. Development and standardization of foundry and fabrication methods.
2. Development of high strength alloys.
3. Development of alloys with greater inherent corrosion resistance.
4. Development of superior protective coatings.

Chapter XXIII.

Nickel.

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While the current history of nickel is largely metallurgical, since this metal is used mainly in the metallic or alloyed form, it appears that comparatively little regarding the metal has been published in American journals during the past year.

Attention may be called to two papers presented at the Congress of Chemists, held in July, 1926. Hatfield[1] described the results of a systematic study of the corrosion-resistance of nickel-bearing steels as compared with plain carbon and 14% chromium steel and Elliot and Willey[2] discussed chemically resistant steels with special reference to their behavior at high and low temperatures.

French[3] has summarized the present available information on the industrial applications of corrosion- and heat-resisting alloys and steels. The nickel-chromium alloys and nickel-bearing steels are among those most commonly used. The nickel-chromium and nickel-chromium-iron alloys and the nickel-chromium steels are particularly adapted for very high temperatures and also for special cases of severe service, such as in the Haber nitrogen fixation process (16% nickel, 16% chromium, 3.5% silicon, balance iron) and the Claude nitrogen fixation process (60% nickel, 12% chromium, balance iron).

Nickel-Bearing Steels for Automobiles. Wickenden[4] has described the compositions, appropriate heat-treatments, properties and automotive applications of the commonly used nickel and nickel-chromium steels, providing systematic data on the subject; very valuable for reference.

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[1] *J. Soc. Chem. Ind.*, **45**, 568 (1926).

[2] *J. Soc. Chem. Ind.*, **45**, 526 (1926).

[3] *Trans. Am. Electrochem., Soc.*, **50**, Preprint (1926).

[4] *Iron Trade Rev.*, 566 (1926).

Nickel Steels in Locomotives. The Canadian Pacific Railroad[5] has recently put into operation forty-four new locomotives extensively equipped with nickel steel parts. Some of these steels are of novel composition, especially developed for locomotive service.

Probably the most interesting feature of these locomotives is the use of high tensile nickel steel boiler plate, used for the first time, at least on locomotives.

By using basic open hearth nickel steel boiler plates, made and rolled by the Lukens Steel Company, specified to have 70,000 psi tensile strength instead of the usual carbon steel with 50,000 psi tensile strength specified, they have been able to increase the boiler pressure from 200 to 250 pounds without any change in the thickness of the plates and secure a substantial increase in tractive power.

In addition novel compositions of nickel steel forgings (main and side rods and crank pins) and of nickel steel frame castings were used on some of these locomotives. These compositions,—containing 2-3% nickel,—were developed especially for locomotive service and with the object of securing maximum toughness and fatigue resistance in large forgings and castings with mild heat-treatment only,—air-quenching or annealing.

Nickel Plating. A better knowledge of the protective value of nickel plating against rusting is being obtained through research work by the U. S. Bureau of Standards which has shown that the protective value of nickel plating increases more than proportionally to the thickness of the deposit. The practice of laying down nickel deposits 0.0001″ to 0.0002″ thick, *i.e.*, about one-tenth of the thickness of tissue paper, or ten to twenty times thinner than an ordinary paint layer, is to be thoroughly condemned, and deposits not less than 0.001″ thick are recommended for all nickel plating specifications.[6]

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[5] *Railway Age*, 82, 928 (1927); Newman and Pascoe, *Iron Age*, 119, 701 (1927).
[6] Turner, *Metal Industry* (London), 30, 253, 263, 291 (1927).

Chapter XXIV.

The Rare Earths.

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Chief Chemist, Welsbach Company

In Volume 1 of this publication detailed reference was made to the discovery by Hopkins of Illinium, the previously undiscovered element No. 61.[1] The announcement of this discovery by Hopkins and his collaborators, Harris and Yntema, brings forth the interesting reminder from Brauner,[2] that veteran authority in rare earth investigations, that as early as 1902 the existence of element No. 61 had been foreshadowed on account of the large atomic weight difference between samarium and neodymium. He further states that it might also have been predicted from the valence of the metals in the hydroxides CsH_1, BaH_2, LaH_3, CeH_4, PrH_3, NdH_2, (XH_1) and SmH_0. In the chemical literature of the year we find that other scientists in various countries have also been independently engaged in a search for this missing element and that too for a period extending over several years. It is interesting to observe the degree of success that had rewarded the labors of these investigators, resulting in some cases in claims for priority in this discovery.

James, who has been engaged in rare earth investigations for many years, has been busy on this problem with his collaborators.[3] These studies were begun in 1923 and were conducted in the Department of Physics of the University of Michigan by Cook, and in the Department of Chemistry of the University of New Hampshire by James and Fogg. Preliminary experiments having given indications of the presence of element No. 61 in gadolinite, xenotime and monazite, a careful examination was made of the minute amount of neodymium which accompanied the yttria earths derived from a large quantity of monazite sand. This was concentrated by fractionally crystallizing the bromates and later the double magnesium nitrates of these earths. This neodymium concentrate was then submitted to an X-ray examination and all of the twenty and more L-series were observed on the photographic plate, seven of which were fairly strong.

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[1] *J. Am. Chem. Soc.*, **48**, 1585, 1594 (1926); *Phys. Rev.*, 25, 106 (1925).
[2] *Nature*, 118, 84 (1926).
[3] *Proc. Nat. Acad. Sci.*, **12**, 696 (1926).

In Germany the work of Meyer, Schumacher and Kotowski, in searching for this element, was reviewed since 1920 and reference made to a dissertation by Schumacher in 1921.[4] Their work was conducted by employing the previously published bromate fractional crystallization method of James in which the missing element tends to concentrate in the less soluble fractions. Further concentration was attained by the fractionation of the magnesium double nitrates with the addition of Mg-Bi double nitrates, a method published by Urbain and Lacombe. The success of their X-ray spectroscopic tests is attributed to the use of the K-series instead of the L-series for identification. Dehlinger, Glocker and Kaupp[5] give heretofore unpublished data of the X-ray measurements of the neodymium-samarium preparations prepared by Meyer as described above. The K spectrum gave three lines of No. 61 which were definitely formed and free from overlapping lines of the accompanying metals. Prandtl[6] recites his own experience in the quest for element No. 61 and gives a rather skeptical criticism of the work of Hopkins and others. Von Welsbach[7] also contributes the results of his own investigations in this search in which he concludes that element No. 61 is not present in detectable quantities in a mixture of neodymium and samarium obtained from cerite.

At the University of Florence, Italy, Rolla and Fernandes and later Brunetti worked on this problem from 1922, recording their results in a sealed note in 1924.[8] The initial investigations were made with a small quantity of material from Brazilian monazite which was rich in neodymium. The L-series of the X-ray spectrum gave negative results but the absorption spectrum giving encouraging indications the experiments were continued with larger quantities of material. After a preliminary separation by the double sulfate method and a double nitrate crystallization with

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[4] *Naturwissenschaften*, **14**, 771 (1926).

[5] *Naturwissenschaften*, **14**, 772 (1926).

[6] *Z. angew. Chem.*, **39**, 897 (1926).

[7] *Chem.-Ztg.*, **50**, 990 (1926).

[8] *Gazz. chim. ital.*, **56**, 435, 688, 862 (1926); *Atti. accad. Lincei*, (6) **4**, 498, 515, 518 (1926); *Z. anorg. allgem. Chem.*, **157**, 371 (1926).

Tl and NH_3 the uncrystallizable residues were transformed to the double nitrates with magnesium and crystallized 3,000 times. From these researches it was claimed that the absorption spectra gave indications of element No. 61. A study of the characteristic K-series absorption spectra showed the presence of a small quantity of element No. 61 in the samarium fraction. The name "Florentium" was proposed by these authors.

W. A. Noyes[9] reviews the published work of Hopkins and his collaborators in comparison especially with that of Rolla and Fernandes and gives the honor for the discovery of element No. 61 primarily to Hopkins, concluding that it should bear the name Illinium.

We are again reminded of the discovery of hafnium by the granting of additional U. S. patents to the discoverers Coster and Hevesy[10] on the method of separating hafnium and zirconium and also to van Arkel and de Boer.[11] De Boer[12] also has secured a patent on certain hafnium and zirconium compounds.

The entire subject of the discovery of new elements is thoroughly reviewed by Bligh[13] in which a description is given of the elements discovered since 1913. The halogen (85) and the alkaline earth (87) with possible elements beyond (92) still await discovery.

Kendall and West[14] have extended Kendall's ionic migration studies to an attempted separation of hafnium and zirconium by this method but the degree of separation was not as great as that obtained with other rare earth metals previously reported upon.

The increasing industrial applications of zirconium particularly in the ceramic industry have resulted in the development of new compounds and processes of manufacture. Kinzie[15] describes a process in which zirconia ore is mixed with an alkali such as Na_2CO_3 and the charge is heated without fusion but sufficiently to effect a decomposition and the formation of a zirconium compound soluble in acids. Kinzie[16] also describes a process in which zirconia ore is fused and the silica is partially expelled from the product which is then mixed with H_2SO_4 at a temperature of 350-450° to obtain a product soluble in acids. He[17] also describes a zirconium oxide-silica compound produced from a zirconium ore such as zircon in which the ore is heated with a smaller quantity of an alkali like Na_2CO_3 at 900° to effect a decomposition. The mass is then treated with H_2SO_4 to obtain a solution containing both zirconium and silicon compounds. The charge is then heated in the presence of sufficient NaCl to precipitate the zirconium compound as a double salt of the alkali metal. This product after drying is suitable for use as a pigment. Le Coultre [18] has described a process for the preparation of refractory products from zirconiferous ores in which the ore is heated to a high temperature in an electric furnace and then is discharged into a violent stream of water charged with one per cent of H_2SO_4. Shearer [19] has conducted extensive experiments with a view of utilizing the white zircon sands of Florida in the ceramic industry without decomposition. Using the Pablo Beach zircon sand he obtains quite satisfactory results by introducing even as high as 70% zircon in some instances. He finds, however, that in general the presence of feldspar is detrimental in a zircon body. The high density of zircon does not seem to preclude its use in casting mixtures. Heany [20] has developed a process for preparing a porous body of highly refractory material for use in electrical apparatus by subjecting this body, such as sintered ZrO_2, to heat in the presence of a molten substance, such as paraffin, which is solid at ordinary temperatures, until the gases in the pores are replaced by the molten substance. When allowed to cool and solidify it is enclosed in a container.

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[9] *Science*, 65, 160 (1927).
[10] U. S. P. 1,618,960 (Feb. 22, 1927).
[11] U. S. P. 1,618,494 (Feb. 22, 1927).
[12] U. S. P. 1,624,162 (April 12, 1927).
[13] *Science Progress*, 21, 109 (1926).
[14] *J. Am. Chem. Soc.*, 48, 2619 (1926).
[15] U. S. P. 1,609,826 (Dec. 7, 1926).
[16] U. S. P. 1,618,286 (Feb. 22, 1927).
[17] U. S. P. 1,618,288 (Feb. 22, 1927).

Prescott, Jr.,[21] has studied the equilibrium between zirconium oxide and carbon and their reaction products at incandescent temperature and has found that the carbide ZrC and not ZrC_2 is the solid product of the reaction. This was confirmed by X-ray powder photographs of the solid products. Free [22] in his investigations of Colorado pitchblends found as high as 5.25% of ZrO_2 but no ThO_2 or other rare earths present. The indications, based on the density of the product obtained, are that this zirconia is of low hafnium content.

During the past year Marden and Rentschler [23] announced the very interesting method devised by them for the preparation of high grade thorium powder, fused metal and ductile thorium metal. After a review of the history of the preparation of thorium powder and a description of their preliminary experiments, they describe their process which consists essentially in the reduction of ThO_2 in an iron bomb by Ca and $CaCl_2$ at 950°C. The proportions are ThO_2 1 part, $CaCl_2$ 1 part and Ca 0.75 part. With a charge sufficient to produce one pound of thorium metal about 1.5 hours was required to raise the temperature to 950°C., where it was maintained from thirty minutes to one hour. After cooling, the bomb is opened and the charge chiseled out and added to a large excess of cool water with agitation. After repeated washings the residue is treated several times with HNO_3 and washed and then is dehydrated with alcohol and ether, sieved, placed in a bottle and the alcohol evacuated. Under good conditions a yield of more than 90% of metal was obtained. In one method of heating, the Th powder is pressed into cylindrical buttons and heated slowly in vacuo in a specially designed high-frequency furnace in order that thorough degasification might be effected before fusion. the button resting on a specially prepared crucible formed from ThO_2. Another special furnace is described for the production of Th wire and Th slugs for use as inserts in X-ray targets. Thorium thus prepared is of great purity, is coherent and is workable, pliable and can be rolled, drawn and worked cold. The sp. gr. is 11.3 — 11.7 depending on previous working. The m. p. is given in this article as 1842 ± 30° in vacuo and in another publication [24] it is given as 2115 K ± 30°. The specific resistance, coefficient of expansion, hardness and tensile strength are also given. The volatility is very low. On account of its high atomic weight Th has been used as an X-ray target. It gives more total X-radiations than tungsten and because of its characteristic K radiation gives deeper penetration in X-ray therapy. Marden [25] has also described a method of reducing refractory metals, such as Zr, Ti, Th, U, W and Mo, by the reduction of their compounds with Mg in an inert environment in a closed container.

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[18] U. S. P. 1,602,273 (Oct. 5, 1926).
[19] *Ceramist*, 5, 316 (1924); *J. Soc. Glass Tech.*, 9, 153 (1925).
[20] U. S. P. 1,592,459 (July 13, 1926).
[21] *J. Am. Chem. Soc.*, 48, 2534 (1926).
[22] *Phil. Mag.*, (7) 1, 950 (1926).
[23] *Ind. Eng. Chem.*, 19, 97 (1927).

Jeffries and Tarsov,[26] after reviewing the conclusions of Langmuir that Th is present in solid solution in thoriated W wires, show by a long series of experiments and microscopic examination that the solid solution of thoria in W wire was not over 0.01%. In electric lamp filaments the thoria particles are useful to control grain growth of the W. They increase slowly in size when the lamp is used, their growth being dependent on diffusion. Thoria is only slightly soluble in liquid W so that the sintering method of producng thoriated W ingots is necessary to secure a uniform distribution of the thoria. The accurate determination of the small quantities of thoria in tungsten filaments is a matter of fundamental importance but is also accompanied with very serious difficulties. Brophy and Van Brunt [27] have developed a process in which W is volatilized in a current of HCl and $CHCl_3$ after a previous oxidation. The residue is assumed to be ThO_2 The problem of determining less than 0.1% Th with certainty is in their judgment not yet solved. Singleton [28] has also given a detailed method for the determination of small amounts of W, Mo and Th.

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[24] *Phys. Rev.*, 25, 589 (1925).
[25] U. S. P. 1,602,542 (Oct. 12, 1926).
[26] *Am. Inst. Mining Met. Eng.*, Preprint No. 1614-E (1927).

Hoover and Rideal [29] have made an extensive study of the decomposition of ethyl alcohol at the surface of thoria and also of the absorption on the thoria catalyst.

James, Fogg, McIntire, Evans and Donovan [30] have reported the results of an extended study of the solubilities in water of the hydrated bromates of La, Pr, Nd, Sm, Gd and Tb of the type $M(BrO_3)_3.9H_2O$. The solubilities of the members of the Ce group are similar and differ somewhat from those of the Tb group. Sarver and Brinton [31] have also determined the solubilities in water of the oxalates of La, Ce, Pr, Nd and Sm. The solubility of these oxalates as well as that of Gd has been determined in solutions of HCl, HNO_3, H_2SO_4, and mixtures of HCl and $H_2C_2O_4$. Zernicke and James [32] have determined the magnetic susceptibilities for Ce, Pr, Nd, Sm, Gd, Tb, Ho, Er and Yb using the improved magnetic balance of the type described by Curie and Chenuveau.

Yntema [33] has developed a theory of color from which he concludes that the presence of color in the rare earths and in some common elements seems to be due to an incomplete atom kernel. He points out some relationships in position of the absorption bands for the rare earths. Meggers [34] also points out some regularities in the arc spectrum of lanthanum. Nichols and Howes [35] published

[27] *Ind. Eng. Chem.*, **19**, 107 (1927).
[28] *Ind. Chemist*, **2**, 454 (1926).
[29] *J. Am. Chem. Soc.*, **49**, 104, 116 (1927).
[30] *J. Am. Chem. Soc.*, **49**, 132 (1927).
[31] *J. Am. Chem. Soc.*, **49**, 943 (1927).
[32] *J. Am. Chem. Soc.*, **48**, 2827 (1926).
[33] *J. Am. Chem. Soc.*, **48**, 1598 (1926).
[34] *J. Wash. Acad. Sci.*, **17**, 25 (1927).
[35] *J. Opt. Soc. Am.*, **13**, 573 (1926).

a report on the effect of the rare earths as activators of luminescence.

It is evident from the brief summary given in the foregoing chapter that much original investigation is now under way in a number of laboratories and further publications may be anticipated in the coming year which the scientific world will await with very keen interest.

Chapter XXV.

Aliphatic Compounds.

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As 70 papers are to be reviewed in a limited space we can do no more than indicate the contents of each article. For convenience they are divided into groups. This year several reports on new industrial processes are included. While these are not strictly the reports of research they show its results and give as much information as we are likely to get about the research itself.

Identification and Estimation. Starr and Gamble[1] have studied the determination of minute amounts of ethyl iodide in air, water and blood. They have attained an accuracy of 2.3% on such small amounts as 0.12 to 2.35 mg. by the use of silver nitrate.

By the use of a triangular diagram which has been worked out, Mortimer[2] determines methanol and ethyl alcohol in water by taking the density and refractive index of the mixture. The percent of water in methanol can be found by its critical solution temperature in ligroin (b. 50-55°) or hexane according to Rising and Hicks.[3] For 2% of water the critical solution temperature is raised from 8.65 to 27.15° for ligroin and from 36.55 to 48.05° for hexane.

Marasco[4] bases a quick method for the estimation of acetone on its reaction with hydroxylamine hydrochloride. The hydrochloric acid liberated in the reaction is titrated.

Elaborate glycerol tables have been prepared by Bosart and Snoddy.[5] The glycerol used had the densities 1.26557 (15/15), 1.26362 (20/20) and 1.26201 (25/25) in air and 1.26526 (15/15), 1.26331 (20/20) and 1.26170 (25/25) reduced to vacuum.

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[1] *J. Biol. Chem.*, **71**, 509 (1927).
[2] *Ind. Eng. Chem.*, **19**, 635 (1927).
[3] *J. Am. Chem. Soc.*, **48**, 1929 (1926).
[4] *Ind. Eng. Chem.*, **18**, 701 (1926).
[5] *Ind. Eng. Chem.*, **19**, 506 (1927).

Determination of the Properties of Organic Compounds. We find 12 papers under this head. There might have been many more as our knowledge of the properties of most compounds is far from exact. Two thorough studies have been made on ethane at the Cryogenic Laboratory of the Bureau of Mines. Porter [6] has measured its vapor pressure and specific volume from its normal boiling point to 288°K., while Loomis and Walters [7] have determined the vapor pressure over a 20° range including the normal boiling point which is 184.467°K. The latent heat of evaporation is 3642.4 cal. per mol.

In a thorough piece of work Tomecko and Adams [8] clear up the long standing uncertainties about the melting points of 5 hydroxystearic acids. They synthesized the 9-, 10-, 11-, 12- and 13-hydroxystearic acids for this purpose.

Noyes and Wobbe [9] find the vapor pressure of anhydrous oxalic acid to be 0.0108 mm. at 60° and 0.537 mm. at 105°. The vapor pressures, densities and heat of evaporation of acetone have been determined by Felsing and Durban.[10] Its density is 0.78612 (25/4). Cox, Nelson and Cretcher [11] have studied the reciprocal solubility of the *n*-propyl ethers of 1,2-propyleneglycol and water. They give closed solubility curves.

The properties of glycol ethers are given by Davidson [12] and those of glycol dinitrate by Rinkenbach.[13] The preparation and properties of diethylene glycol are described by Rinkenbach.[14] The properties and reactions of tertiary alcohols are discussed by Davis and Murray.[15]

The viscosities of water solutions of methyl and ethyl acetates, ether and benzene have been measured by Chadwell.[16]

The heat capacities, entropies and free energies of *n*-propyl alcohol, ether and dulcitol have been studied by Parks and Huffman.[17]

Determination of Composition and Constitution of Natural Substances. As constituents of the cotton plant, ammonia, trimethylamine, quercetin, formic, acetic, palmitic and succinic acids, betaine, choline, pentatriaconatane, dipentene and a sesquiterpene have been identified by Power and Chestnut.[18]

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[6] *J. Am. Chem. Soc.*, **48**, 2055 (1926).
[7] *J. Am. Chem. Soc.*, **48**, 2051 (1926).
[8] *J. Am. Chem. Soc.*, **48**, 522 (1927).
[9] *J. Am. Chem. Soc.*, **48**, 1882 (1926).
[10] *J. Am. Chem. Soc.*, **48**, 2885 (1926).
[11] *J. Am. Chem. Soc.*, **49**, 1080 (1927).
[12] *Ind. Eng. Chem.*, **18**, 669 (1926).
[13] *Ind. Eng. Chem.*, **18**, 1195 (1926); *Chem. Met. Eng.*, **34**, 296 (1927).
[14] *Ind. Eng. Chem.*, **19**, 474 (1927).
[15] *Ind. Eng. Chem.*, **18**, 844 (1926).
[16] *J. Am. Chem. Soc.*, **48**, 1912 (1926).
[17] *J. Am. Chem. Soc.*, **48**, 2788 (1926).

Nelson[19] has found citric and malic acid in Bartlett pears, *l*-malic and a trace of citric in winesap apples, citric and *l*-malic in loganberries and blueberries, cranberries and California lemons but only citric in pomegranate.

Beath[20] has studied the natural occurrences of aconitic acid and its isomers. At least two forms are found.

Chinese wood oil has been investigated by Rhodes and Welz.[21] Over 90% of the oil is a glyceride of eleomargaric acid. The oil polymerizes on heating and gelatinizes when the average molecular weight reaches 1700.

Shriner, Nabenhauer and Anderson[22] find corn wax to be a mixture of the myricyl esters of *n*-tetracosanoic and isobehenic acids. Tourtellotte and Hart[23] find in ovarian fat myristic, palmitic, stearic, oleic, linoleic, arachidic acids and triunsaturated acid.

According to Jodidi[24] tyrosine, leucine, myristic, palmitic and stearic acids are among the products of the action of *Bacterium pruni* on milk.

Fish oils have been studied by McGregor and Beal[25] who find a remarkable regularity in the unsaturation of the acids present. There can be 3 double bonds in a C_{16} acid, 4 in a C_{18}, 5 in a C_{20} and 6 in a C_{22} acid. The first double bond is at C_9; the others follow on the odd numbered carbons. There is never a double bond between the last two carbons.

The composition of petroleum has been further studied by Mabery[26] and that of gasoline by Hill, Henderson and Ferris.[27]

Preparation of Compounds. Various catalysts have been tried by Schuette and Sah[28] in the preparation of monoacetin. Phosphoric acid proved to be the best. The same authors[29] improve the method of making *n*-valerolactone. Three hydroxyaminovaleric acids have been prepared by Osterberg.[30] A new synthesis of β-hydroformamine cyanide has been found by Rinehart.[31]

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[18] *J. Am. Chem. Soc.*, **48**, 2721 (1926).
[19] *J. Am. Chem. Soc.*, **49**, 1300 (1927).
[20] *J. Am. Chem. Soc.*, **48**, 2155 (1926).
[21] *Ind. Eng. Chem.*, **19**, 68 (1927).
[22] *J. Am. Chem. Soc.*, **49**, 1290 (1927).
[23] *J. Biol. Chem.*, **71**, 1 (1926).
[24] *J. Am. Chem. Soc.*, **49**, 1556 (1927).
[25] *J. Am. Chem. Soc.*, **48**, 3150 (1926).
[26] *Ind. Eng. Chem.*, **18**, 814 (1926).
[27] *Ind. Eng. Chem.*, **19**, 128 (1927).
[28] *J. Am. Chem. Soc.*, **48**, 3161 (1926).
[29] *J. Am. Chem. Soc.*, **48**, 3163 (1926).
[30] *J. Am. Chem. Soc.*, **49**, 538 (1927).
[31] *J. Am. Chem. Soc.*, **48**, 2794 (1926).

Isopropyl- and butyltrichloromethyl carbinols and their esters have been made by Howard.[32] The manufacture of amyl acetate from chlorinated pentane is described by Koch and Burrell,[33] and also by Kirkpatrick.[34] The latter writer [35] gives an account of developments in the manufacture of isopropyl alcohol. Hoffman [36] finds that ethers of diacetone alcohol can be obtained by the addition of the alcohols to mesityl oxide. These ethers cannot be prepared by the usual methods. The lithium, sodium, rubidium and cesium salts of azidodithiocarbonic acid have been prepared by Browne and Audrieth.[37] Pure cysteine, having a specific rotation of + 9.7°, has been obtained by Andrews [38] by the reduction of *l*-cystine. The manufacture of oxalic, lactic and formic acids is described by Kirkpatrick.[39]

Reactions of Compounds. Cantelo [40] has discussed the stability of hydrocarbons to heat and concludes that any hydrocarbon will ultimately give an equilibrium mixture of methane, carbon and hydrogen. Wobbe and Noyes [41] have studied the thermal and photochemical decomposition of oxalic acid. The decomposition velocities of diacetone alcohol in alkaline solutions containing salts have been measured by Åkerlöf.[42] The action of alkyl halides on acetamide at 220° has been tried by Nicholas and Erickson. The *N*-alkyl amide is obtained in good yield and from this monoalkyl amines are readily obtained. The reversible cysteine-cystine system has been studied by Kendall and Nord.[43] Levene and Walti [44] have reacted propylene oxide with ammonia. The decomposition of azomethane has been found by Ramsperger [45] to be homogeneous at all pressures but strictly unimolecular only at high pressures. Mesityl oxide has been condensed with various ketones by Ekeley and Carpenter.[46] Only one product is formed with each ketone.

The polymerization of linseed oil in the boiling process has been measured by Long, Knauss and Smull.[47] Brown and Snyder [48] show that ethyl mercaptan is formed from ethyl iodide and hydrogen sulfide in water, the rate decreasing as the hydrogen ion concentration increases. The reaction is favored by the presence of metal sulfides and of adsorbents.

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[32] *J. Am. Chem. Soc.*, **49**, 1068 (1927).
[33] *Ind. Eng. Chem.*, **19**, 442 (1927).
[34] *Chem. Met. Eng.*, **34**, 276 (1927).
[35] *Chem. Met. Eng.*, **33**, 402 (1926).
[36] *J. Am. Chem. Soc.*, **49**, 530 (1927).
[37] *J. Am. Chem. Soc.*, **49**, 917 (1927).
[38] *J. Biol. Chem.*, **69**, 209 (1926).
[39] *Chem. Met. Eng.*, **33**, 423 (1926).
[40] *J. Phys. Chem.*, **31**, 124, 246 (1927).
[41] *J. Am. Chem. Soc.*, **48**, 2856 (1926).
[42] *J. Am. Chem. Soc.*, **48**, 3046 (1926).
[43] *J. Biol. Chem.*, **69**, 295 (1926).
[44] *J. Biol. Chem.*, **71**, 461 (1927).
[45] *J. Am. Chem. Soc.*, **49**, 912, 1495 (1927).
[46] *J. Am. Chem. Soc.*, **48**. 2375 (1926).
[47] *Ind. Eng. Chem.*, **19**, 62 (1927).
[48] *J. Am. Chem. Soc.*, **48**, 1926 (1927).

The reactivity of chlorinated ether with zinc is considered in the light of the polar conception of valence by Neher and Fleece.[49] The action of zinc is selective. The reaction of caustic potash on *dl*-glyceric aldehyde has been investigated by Evans and Hass.[50] They improve the preparation of acrolein. Evans and Waring[51] oxidize dihydroxyacetone to hydroxypyruvic aldehyde which is isolated in the trimeric form melting at 99°. Fry and Cameron[52] have experimented with sodium methylate as a reducing agent. Simons[53] has passed triacetin at 460-525° and tripropionin at 420-510° over thoria and isolated the decomposition products. Formic acid, in relatively large amounts, results from the decomposition of the triacetin and acetic acid from the other ester.

The action of bromine on lubricant hydrocarbons from petroleum has been studied by Mabery.[54] He finds substitution but no addition and concludes that these hydrocarbons are saturated although they have the general formula C_nH_{2n-4}. The effect of heat on petroleum oils is thoroughly investigated by Leslie and Potthoff.[55] Many factors have been varied and their influence noted.

Lind and Bardwell[56] have subjected methane and other hydrocarbons to the action of alpha particles. Mixtures of higher and lower hydrocarbons are obtained. These are much the same regardless of the hydrocarbon from which they are produced.

Constitution and Properties. Five amylenes have been prepared by Norris and Joubert.[57] These have been compared as to their rates of polymerization, in the presence of sulfuric acid, so as to bring out the relation of these rates to constitution of the hydrocarbons. The mechanism of polymerization is discussed. Jones and Major[58] have prepared a number of *o*-alkylhydroxylamines analogous to cholin, procaine, veronal, etc., and have found that the physiological effects of the corresponding compounds are similar though different in degree.

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[49] *J. Am. Chem. Soc.*, **48**, 2416 (1926).
[50] *J. Am. Chem. Soc.*, **48**, 2703 (1926).
[51] *J. Am. Chem. Soc.*, **48**, 2678 (1926).
[52] *J. Am. Chem. Soc.*, **49**, 864 (1927).
[53] *J. Am. Chem. Soc.*, **48**, 1991 (1926).
[54] *J. Am. Chem. Soc.*, **48**, 2663 (1926).
[55] *Ind. Eng. Chem.*, **18**, 776 (1926).
[56] *J. Am. Chem. Soc.*, **48**, 2335 (1926).
[57] *J. Am. Chem. Soc.*, **49**, 873 (1927).
[58] *J. Am. Chem. Soc.*, **49**, 1527 (1927).

Bennett and Daniels [59] have found an absorption band near 5.90μ in the spectra of the various chloroacetic acids. This shifts 0.05μ for each chlorine that is put in. The absorption spectra of ethyl ether, methyl *n*-amyl ether, ethylene, chlorohydrin and benzene have been compared by Smith, Boord, Adams and Pease.[60] They find certain bands common to all of these and conclude that these are characteristic of the carbon-hydrogen linkage.

Smith and Boone [61] have added the acids of the acetic acid series to rubber and found that the effects are greater or less according to whether the acid contains an even or odd number of carbon atoms.

Theory of Organic Compounds and of Reactions. The structure of hydroxyureas and of carbamazides have been investigated by Hurd and Spence,[62] who find them to be $R_2N—CO—NHOH$ and $R_2N—CO—N_3$. Their rearrangements are considered. Hager and Marvel [63] conclude that the fifth valence of nitrogen, in its quarternany compounds, is unique. The ionization potential of methane has been measured by Glockler.[64] The value found, 14.4 to 15.2 volts, indicates a rare-gas arrangement of electrons similar to krypton. The adsorption of light is used by Acly and French [65] as an aid in the study of the constitution of diketones. We find an important series of papers by Levene and his coworkers, Haller, Mikeska, Walti, Bass, Steiger and Bencowitz,[66] on the relation of configuration to the optical activity of hydroxy compounds, mercaptans, sulfonic acids, etc., including a study of the Walden inversion.

SUGGESTED RESEARCH

In aliphatic chemistry, as elsewhere, we are always in need of improved methods of preparation, purification and identification with more exact determinations of physical constants. There is usually a sad falling off in our knowledge when we get beyond the lower members of any series. In this division of chemistry the ideas of series and isomerism are of the greatest importance. We need more thorough comparisons of the members of any given series, not of one or two but of a large enough number to characterize the series as a whole. We need better methods of preparing members of most series from C_5 on up.

Many new compounds are becoming available on a commercial scale. These give many opportunities for synthesis and study of the compounds thus formed.

A proper utilization of aliphatic hydrocarbons is an outstanding problem which is ever with us.

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[59] *J. Am. Chem. Soc.*, **49**, 50 (1927).
[60] *J. Am. Chem. Soc.*, **49**, 1335 (1927).
[61] *Ind. Eng. Chem.*, **19**, 398 (1927).
[62] *J. Am. Chem. Soc.*, **49**, 266 (1927).
[63] *J. Am. Chem. Soc.*, **48**, 2689 (1926).
[64] *J. Am. Chem. Soc.*, **48**, 2021 (1926).
[65] *J. Am. Chem. Soc.*, **49**, 847 (1927).
[66] *J. Biol. Chem.*, **69**, 165, 569 (1926); **70**, 365 (1926); **71**, 465 (1927); **72**, 591, 815 (1927); **73**, 263 (1927).

RESEARCH BY INSTITUTIONS

Universities and Colleges	*Types of Compounds*	*Investigators*
California	Decompn. of azomethane	H. C. Ramsperger
California Inst. Tech.	Ioniz. pot. of methane	G. Glockler
Case School	Petroleum hydrocarbons	Chas. F. Mabery
Chicago	Decompn. of oxalic acid	W. A. Noyes, Jr., D. E. Wobbe
	Methyl alcohol	Mary M. Rising, J. S. Hicks
Cincinnati	Sodium methylate	H. S. Fry, J. L. Cameron
	Decompn. of hydrocarbons	R. C. Canteio
Colorado	Mesityl oxide	J. B. Ekeley, M. S. Carpenter
Cornell	Azido-dithiocarbonic acid	A. W. Browne, L. F. Andrieth
	Chinese wood oil	F. H. Rhodes, C. J. Welz
Illinois	Quarternary N compds.	F. D. Hager, C. S. Marvel
	Hydroxystearic acids	C. G. Tomecko, R. Adams
	Unsatd. acids	R. R. McGregor, G. D. Beal
Illinois Wesleyan	Mixtures of alcohols	F. S. Mortimer
Iowa State	Mercaptan	F. E. Brown, J. E. Snyder
Lehigh	Polymerization	J. S. Long, C. A. Knauss, J. G. Small
Mass. Inst. Tech.	Amylenes	J. F. Norris, J. M. Joubert
Michigan	Cracking hydrocarbons	E. H. Leslie, E. H. Potthoff
Montana	Alcohols and esters	J. W. Howard
Northwestern	Hydroxyurea	C. D. Hurd, L. V. Spence
Ohio	Glyceric aldehyde	W. L. Evans, H. B. Hass

RESEARCH BY INSTITUTIONS—*Continued*

Universities and Colleges	*Types of Compounds*	*Investigators*
	Dihydroxyacetone	W. L. Evans, C. E. Waring
	Absorption spectra	C. E. Boord, C. S. Adams, C. S. Pease
Pennsylvania	Estn. of ethyl iodide	I. Starr, Jr., C. J. Gamble
	Cysteine	J. C. Andrews
	Diacetone alcohol	G. Åkerlöf
Pittsburgh	Glycol ethers	H. L. Cox, W. L. Nelson, L. H. Cretcher
Princeton	Chlorinated ether	F. Nehr, C. L. Fleece
	Hydroxylamine derivs.	L. W. Jones, R. T. Major
Rice	Amides	H. O. Nicholas, J. L. E. Erickson
Stanford	Heat capacities, etc.	G. S. Parks, H. M. Huffman
Texas	Properties of acetone	W. A. Felsing, S. A. Durban
Tufts	Viscosities of solutions	H. M. Chadwell
Wellesley	Absorption spectra	H. E. Acly, H. S. French
Wisconsin	Absorption spectra	W. H. Bennett, F. Daniels
	Valerolactone	H. A. Schuette
	Monacetin	P. P. T. Sah
Wyoming	Aconitic acid	O. A. Beath
Yale	Hydroformamine compounds	H. W. Rinehart
	Decompn. of glycerides	F. L. Simmons
Research Institutes etc.		
Bureau of Chemistry	Cotton plant	F. B. Power, V. K. Chestnut
	Fruit acids	E. K. Nelson

RESEARCH BY INSTITUTIONS—*Continued*

Research Institutes, etc.	*Types of Compounds*	*Investigators*
Bureau of Mines	Glycol derivatives	W. H. Rinkenbach
	Ethane	F. Porter, A. G. Loomis, J. E. Walters
Bureau Plant Industry	Milk products	S. L. Jodidi
Bureau Standards	Aliphatic acids	W. H. Smith, C. E. Boone
Fixed Nitrogen Lab.	Decompn. methane by α-particles	S. C. Lind, D. C. Bardwell
Kew Gardens	Diacetone alcohol	A. Hoffman
Mayo Foundation	Cystein-cystine equil.	E. E. Kendall, F. F. Nord
	Hydroxyamino acids	A. E. Osterberg
New York Exp. Station	Corn wax	R. L. Shriner, F. P. Nabenhauer, R. J. Anderson
Rockefeller Inst.	Configurations of opt. act. compds.	P. A. Levene, H. L. Haller, A. Walti, L. W. Bass, R. F. Steiger, I. Bencowitz, L. A. Mikeska
Industrial Laboratories		
Atlantic Refining Co.	Gasoline constituents	J. B. Hill, L. M. Henderson, S. W. Ferris
Carbide and Chemicals Co.	Glycol ethers	J. G. Davidson
DuPont-Pathe	Estn. of acetone	M. Marasco
A. D. Little, Inc.	Tertiary alcohols	H. S. Davis, W. J. Murray
Proctor and Gamble	Glycerol	L. W. Bosart, A. O. Snoddy
Upjohn Co.	Ovarian fats	D. Tourtellotte, M. C. Hart

Chapter XXVI.

Carbocyclic Series.

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Eliminating those investigations involving organometallic compounds such as the Grignard reagent, those on azo and anthraquinone dyes, explosives, and those falling into other special chapters, a very heterogeneous group of papers which are difficult to classify is left for review under the heading carbocyclic series. Certain compounds containing an aromatic nucleus have not been reviewed when merely the aliphatic part of the molecule is involved.

A number of investigations have been published which are of general interest to the chemistry of dyes or to the dye industry. Brode and Adams[1] have continued their work on optically active dyes and the mechanism of dyeing and a careful comparison of certain enantiomorphic forms has failed to establish any difference in the dyeing properties. Results of other investigators which led to the opposite conclusion were shown to be incorrect.

Piccard[2] has extended his work on substances having a color of the second order. He has modified his original definition so that it now reads as follows: "Any colored compound has a color of the second order if it has very strong absorption in the infra red next to the visible part of the spectrum." The mono- and di-holoquinoid salts of dimethyldiphenyl-*p*-phenylenediamine have been studied and the meri-quinoid salts of the biphenyl derivatives of *p*-phenylenediamine and of benzidine.

Anderson and Nabenhauer[3] have demonstrated that the anthocyanin in Isabella grapes is oenin; Holmes and Scanlan[4] have discussed the constitution of erythrosin and similar substances;

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[1] Brode and Adams, *J. Am. Chem. Soc.*, 48, 2193, 2202 (1926).
[2] Piccard, *J. Am. Chem. Soc.*, 48, 2352, 2355, 2878 (1926).
[3] Anderson and Nabenhauer, *J. Am. Chem. Soc.*, 48, 2997 (1926).
[4] Holmes and Scanlan, *J. Am. Chem. Soc.*, 48, 1594 (1926).

Brode[5] has described the absorption spectra of benzeneazobenzene; Orndorff[6] and his associates, Fuchs, McNulty, Purdy, Johnson, Lacey, Esselstyn, Hemmer, Wang, Gibbs, Shapiro have continued their work on the preparation and structure of various phthaleins, sulfonephthaleins and related compounds, and have determined the absorption spectra of a large number of them; Phillips[7] has described the condensation of phthalic anhydride with 1,4- and 1,2-dichlorobenzenes to yield the corresponding benzoylbenzoic acids. These were then converted to the 1,4-dichloroanthraquinone and 2,3-dichloroanthraquinone respectively. It is of interest that the latter upon fusion with alkali gives alizarin, due undoubtedly to rearrangement; Heid[8] has demonstrated that 2,7-naphthalenedisulfonic acid rearranges to a considerable extent to the 2,6 modification at 160°; a process for purification of the 2,7 compound is described; Puntambeker and Adams[9] have extended their work on the preparation of polyhydroxyanthraquinones through the use of opianic acid and have synthesized hydroxyanthrarufin and rufiopin, thus establishing their structures without question; Johnson and Staub[10] have offered a new green food dye which has passed the required tests. It has been called Fast Green F.C.F. and is a triphenylmethane derivative made by condensing *p*-hydroxybenzaldehyde-*o*-sulfonic acid with two molecules of ethylbenzylaniline-*o*-sulfonic acid and then oxidation of the leuco base; Conant and Pratt[10a] have studied the reduction of azo dyes under various conditions.

The number of papers which have had as their object the preparation of substances of pharmacological importance is large. In the field of local anesthetics McElvain[11] has described 1-alkyl-3-carbethoxy-4-piperidyl benzoates and *p*-aminobenzoates. These appear to be effective anesthetics and show the peculiarity of decrease in toxicity and increase in activity by increase of the size of the alkyl group attached to the nitrogen; Hill and Cox[12] have prepared ester substituted amidines of the holocaine type; Heckel and Adams[13] have prepared cyclamine esters of *p*-aminobenzoic acid and Barnes and Adams [14] the piperidyl and carboethoxypiperidyl esters of *p*-aminobenzoic acid; Vliet and Adams [15] have determined the relationship between hydrogen ion concentration and chemical constitution in certain local anesthetics; Jones and Major [16] have made substances analogous to procaine in which the diethylamino radical is replaced by *O*-alkyl hydroxylamine; Thayer [17] has described molecular compounds of anesthesin and its homologs with picric acid to be used as antiseptic-anesthetics.

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[5] Brode, *J. Am. Chem. Soc.*, **48**, 1984 (1926).

[6] Orndorff, *J. Am. Chem. Soc.*, **48**, 1939, 1994, 2212, 2221 (1926); **49**, 818, 826, 992, 1272, 1284, 1541, 1545, 1588 (1927).

[7] Phillips, *J. Am. Chem. Soc.*, **48**, 3198 (1926); **49**, 473 (1927).

[8] Heid, *J. Am. Chem. Soc.*, **49**, 844 (1927).

[9] Puntambeker and Adams, *J. Am. Chem. Soc.*, **49**, 486 (1927).

[10] Johnson and Staub, *Ind. Eng. Chem.*, **19**, 497 (1927).

[10a] Conant and Pratt, *J. Am. Chem. Soc.*, **48**, 2468 (1926).

[11] McElvain, *J. Am. Chem. Soc.*, **48**, 2179, 2239 (1926).

[12] Hill and Cox, *J. Am. Chem. Soc.*, **48**, 3214 (1926).

[13] Heckel and Adams, *J. Am. Chem. Soc.*, **49**, 1303 (1927).

More papers on antiseptics analogous to hexyl resorcinol have appeared. Twiss [18] has described caproylresorcinol, and Klarmann,[19] certain dialkyl resorcinols; Feirer and Leonard [20] have demonstrated the stability of hexylresorcinol.

Bogert and Taylor [21] have prepared a number of new derivatives of phenacetin; Keach and Hill [22] have described a variety of acetophenonyl derivatives of barbituric acid; McCluskey and Sher [23] have synthesized the menthyl esters of benzoic, cinnamic and certain substituted cinnamic acids for study in the chemotherapy of *B. tuberculosis;* Chen and Kao [24] have made a careful study of the isolation, purification and physical properties of ephedrin and pseudoephedrin; Mills [25] has given improved details for preparing phenyl esters of salicylic acid; Nightingale,[26] details for preparing acetyl salicylic acid from salicylic acid and ketene; and Gubelmann, Weiland and Stallmann,[27] details for guaiacol from diazo-*o*-phenol in the presence of copper phosphate and absence of sulfuric acid.

In continuation of the work on chaulmoogric acid and related compounds Hiers and Adams [28] have prepared the ω-cyclohexyl derivatives of a series of normal aliphatic acids, and have shown that many of these acids are bactericidal toward *B. leprae,* the acids containing 8 and 9 carbon atoms in the side chain being the most effective; VanDyke and Adams [29] have prepared chaulmoo-

[14] Barnes and Adams, *J. Am. Chem. Soc.,* **49**, 1307 (1927).
[15] Vliet and Adams, *J. Am. Chem. Soc.,* **48**, 2158 (1926).
[16] Jones and Major, *J. Am. Chem. Soc.,* **49**, 1527 (1927).
[17] Thayer, U. S. P. 1,596,259 (Aug. 17, 1926).
[18] Twiss, *J. Am. Chem. Soc.,* **48**, 2206 (1926).
[19] Klarmann, *J. Am. Chem. Soc.,* **48**, 2358 (1926).
[20] Feirer and Leonard, *J. Pharmacol.,* **28**, 395 (1926).
[21] Bogert and Taylor, *J. Am. Chem. Soc.,* **49**, 1578 (1927).
[22] Keach and Hill, *J. Am. Chem. Soc.,* **48**, 2743 (1926).
[23] McCluskey and Sher, *J. Am. Chem. Soc.,* **49**, 452 (1927).
[24] Chen and Kao, *J. Am. Pharm. Assoc.,* **15**, 625 (1926).
[25] Mills, U. S. P. 1,606,171 (Nov. 9, 1926).
[26] Nightingale, U. S. P. 1,604,472 (Oct. 26, 1926).
[27] Gubelmann, Weiland and Stallmann, U. S. P. 1,623,949 (Apr. 5, 1927).
[28] Hiers and Adams, *J. Am. Chem. Soc.,* **48**, 2385 (1926).
[29] VanDyke and Adams, *J. Am. Chem. Soc.,* **48**, 2393 (1926).

grylacetic acid; Sacks and Adams [30] homohydnocarpic and homochaulmoogric acids and certain chaulmoogrylamines; Noller and Adams [31] have synthesized Δ^2-cyclopentenylethanol to be used as a raw material for building up ω-cyclopentenyl aliphatic acids. In this same field Perkins and Cruz [32] have synthesized a number of Δ^2-cyclopentenyl alkyl acetic acids and the *dl*-modification of chaulmoogric acid. That the structure of the latter substance though not optically active was the same as that of the natural chaulmoogric acid was proved by oxidation and isolation of the same decomposition products.

Two articles have been contributed to the study of the structure of substituted diphenyl and 2,7-di-substituted naphthalene. Gilman and Kirby [33] have attempted to rearrange biphenylhydroxylamine in the hope that the hydroxyl might take the vacant para position in the unsubstituted benzene ring. This was unsuccessful, however; Raiford and Talbot [34] have attempted to apply their methods for rearranging certain acylated *o*-aminophenols to 2-amino-7-hydroxynaphthol. The latter substance, however, does not act like an *o*-aminophenol.

A number of papers involving the determination of the structure of certain compounds have been published. Levine [35] has chlorinated 2,6-pyrogallol methyl ether and shown that the first chlorine enters meta to the hydroxyl group; Rice [36] has proved the position of the bromine in bromo-2,4-dimethoxybenzoic acid. Moore and Tucker [37] have discussed the previous work on the sulfonation of cinnamic acid and have shown definitely that the product is the *m*-compound; sodium bisulfite was added to cinnamic acid and its derivatives; Raiford and Stoesser,[38] and Raiford and Hilman [39] have made a careful study of the synthesis and structure of bromine derivatives of vanillin.

Fierer [40] has made a study of "Naphthalenic acid," hydroxynaphthoquinone, and has shown that the acid consists of a mixture of tautomers, 2-hydroxy-1,4-naphthaquinone and 4-hydroxy-1,2-naphthaquinone. Upon methylation under various conditions he

[30] Sacks and Adams, *J. Am. Chem. Soc.*, **48**, 2395 (1926).
[31] Noller and Adams, *J. Am. Chem. Soc.*, 48, 2444 (1926).
[32] Perkins and Cruz, *J. Am. Chem. Soc.*, **49**, 517, 1070 (1927).
[33] Gilman and Kirby, *J. Am. Chem. Soc.*, **48**, 2190 (1926).
[34] Raiford and Talbot, *J. Am. Chem. Soc.*, **49**, 559 (1927).
[35] Levine, *J. Am. Chem. Soc.*, **48**, 2719 (1926).
[36] Rice, *J. Am. Chem. Soc.*, **48**, 3125 (1926).
[37] Moore and Tucker, *J. Am. Chem. Soc.*, **49**, 258 (1927).
[38] Raiford and Stoesser, *J. Am. Chem. Soc.*, 49, 1077 (1927).
[39] Raiford and Hilman, *J. Am. Chem. Soc.*, 49, 1571 (1927).
[40] Fierer, *J. Am. Chem. Soc.*, 48, 2922, 3201 (1926); 49, 857 (1927).

was able to obtain *o*- and *p*-quinone *O*-ethers and in certain instances carbon-alkylation. By the use of the proper halides a substance was obtained which appears to be identical with lapachol, the yellow coloring matter occurring in the grains of various kinds of wood.

A few papers of interest in analytical work have been published. Riegel and Williams [41] have described a color reaction for procaine and certain other anesthetics of a similar type. It consists in the treatment of procaine with nitrous acid and then with ammonia giving an intense yellow color. It serves to distinguish procaine in the presence of a large number of the alkaloids which frequently occur in a pharmaceutical mixture; Marvel and Gillespie [42] have described a series of benzylsulfonamides prepared from benzylsulfone chloride and various amines. These derivatives appear to be useful for the identification of certain amines; Schultz and Lucas [43] have described in detail the sulfonation of *o*-toluidine and have offered improved conditions for converting the product to sodium 6-chloro-5-nitro-*m*-toluene-sulfonate, a reagent useful for separating potassium and rubidium from lithium, sodium and cesium; Glattfeld, Hopkins and Thurber [44] have prepared *p*-trimethylethylbenzoyl chloride and Glattfeld and Cameron,[45] *p*-active-amylphenylhydrazine, both being reagents which these investigators hope to use in the resolution of certain sugars or their derivatives; Hopkins [46] has shown that easily reduced manganese salts produce the characteristic chlorine color with *o*-tolidine; Williams [47] has described details for the determination as tribromophenol of phenol in ammonia liquors.

A number of synthetic processes or improvements in those already described have been reported. Smith and Lyons [48] have found that benzyl alcohol can be oxidized to benzoic acid by means of nitrobenzene or nitrotoluene; Gebauer-Fülnegg [49] has shown that aluminum amalgam in alcohol and ether is an excellent agent for reducing sulfone chlorides to mercaptans; Bacharach [50] has made a careful study of the nitration of various aromatic compounds by means of different metallic nitrates and acetic anhydride. He has found that there is a certain specificity in many cases not only in regard to the ease of nitration but also in regard to the position taken by the nitro group; Rising and Zee[51] have described what they claim to be a better procedure than any previously published for preparing methyl phenylethylmalonate, an intermediate used in the preparation of phenobarbital; Pratt, Weltz and Mills[52] have discovered that in converting *o*-nitrochlorobenzene or analogous compounds to *o*-nitroanisol by means of methyl alcoholic potassium hydroxide, oxygen or air under pressure prevents the reduction of the nitro group; Hale and Britton[53] have described the preparation of phenol from chlorobenzene and alkali in the presence of oxides of metals of groups V and VI and in the presence of diphenyl ether; they also describe the conversion of chlorobenzene to aniline by ammonia and copper or certain copper salts; Homolka[54] has condensed acetone with two molecules of aniline hydrochloride to give di-(*p*-aminophenyl) dimethylmethane; Heinze,[55] *p*-phenylenediamine and urea in an inert solvent to give diaminodiaryl ureas; Wahl[56] has described the separation of *o*-chlorotoluene from the *p*-isomer by sulfonation; Herz and Schulte,[57] the preparation of 1,8-hydroxynaphthoic acid.

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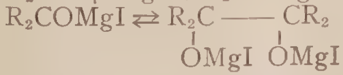
[41] Riegel and Williams, *J. Am. Chem. Soc.*, **48**, 2871 (1926).
[42] Marvel and Gillespie, *J. Am. Chem. Soc.*, **48**, 2943 (1926).
[43] Schultz and Lucas, *J. Am. Chem. Soc.*, **49**, 298 (1927).
[44] Glattfeld, Hopkins and Thurber, *J. Am. Chem. Soc.*, **49**, 1039 (1927).
[45] Glattfeld and Cameron, *J. Am. Chem. Soc.*, **49**, 1043 (1927).
[46] Hopkins, *Ind. Eng. Chem.*, **19**, 744 (1927).
[47] Williams, *Ind. Eng. Chem.*, **19**, 530 (1927).
[48] Smith and Lyons, *J. Am. Chem. Soc.*, **48**, 3165 (1926).
[49] Gebauer-Fülnegg, *J. Am. Chem. Soc.*, **49**, 1386 (1927).
[50] Bacharach, *J. Am. Chem. Soc.*, **49**, 1522 (1927).

One of the most interesting papers published during the year is that by Gomberg and Bachmann[58] on the reducing action of a mixture of magnesium and magnesium iodide on aromatic ketones. The evidence is in favor of the primary formation of magnesium sub-iodide. This combines with the ketone to give a free radical which then associates to a pinacol derivative. The following equations illustrate what probably happens:

$$Mg + MgI_2 \leftrightarrows 2MgI$$

$$R_2CO + MgI \leftrightarrows R_2COMgI$$



$$R_2COMgI \rightleftarrows \underset{\displaystyle OMgI}{\underset{|}{R_2C}} - \underset{\displaystyle OMgI}{\underset{|}{CR_2}}$$

Promising results may be anticipated from this reagent in the reduction of other types of organic compounds.

The Friedel and Crafts reaction has been studied in a number of different synthetic processes. Huston and Sager,[59] and Huston, Lewis and Grotemut[60] have condensed various types of alcohols with benzene in the presence of anhydrous aluminum chloride to give substituted benzenes. It has been found that when the hydroxyl group is on the carbon atom attached to the ring or when the hydroxyl is in the proper relative position to an olefine group as in allyl alcohol, the reaction goes smoothly but in other positions the alcohols do not condense at all. Harris and Frankforter[61] have condensed chloral and bromal with benzene and with phenol ethers. Two molecules of the aromatic compound reacted with the chloral or bromal with the elimination of a molecule of water and the formation of an unsymmetrical diphenylethane derivative. The chemical reactions of these products have been studied and of particular note may be mentioned that sodium converts them to stilbenes and alcoholic potash to unsymmetrical dichloro olefins; Cox[62] has described conditions for the action of anhydrous aluminum chloride on cresyl benzoates with the formation of benzoylcresols; Nicolet and deMilt[63] have condensed oleic acid with benzene in the presence of anhydrous aluminum chloride and thus obtained a phenylstearic acid, the exact constitution of which was not determined.

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[51] Rising and Zee, *J. Am. Chem. Soc.*, 49, 541 (1927).

[52] Pratt, Weltz and Mills, U. S. P. 1,619,368 (Mar. 1, 1926).

[53] Hale, U. S. P. 1,595,299 (Aug. 10, 1926); Hale and Britton, 1,607,618, 1,607,824 (Nov. 23, 1926).

[54] Homolka, U. S. P. 1,591,384 (July 6, 1926).

[55] Heinze, U. S. P. 1,617,847 (Feb. 15, 1927).

[56] Wahl, U. S. P. 1,596,325 (Aug. 17, 1926).

[57] Herz and Schulte, U. S. P. 1,623,678 (Apr. 5, 1927).

[58] Gomberg and Bachmann, *J. Am. Chem. Soc.*, 49, 236 (1927).

Berliner and May[64] and May, Berliner and Lynch[65] have continued their study of the vapor pressures of organic compounds and have selected for their present researches nitrotoluenes, toluidines and naphthols; the latent heat equations have been derived. Klosky, Woo and Flanigan[66] have determined the vapor pressure of benzoic acid.

Smyth and Morgan[67] have continued the work on the electric moments of substituted benzene molecules and have discussed the structure of benzene.

In the field of catalysis, Reiff[68] has studied various factors which effect the oxidation of benzaldehyde by atmospheric oxygen; Stephens[69] has studied the effect of gaseous oxygen on various aromatic hydrocarbons at about 100°. He found that the oxidation

[59] Huston and Sager, *J. Am. Chem. Soc.*, 48, 1955 (1926).
[60] Huston, Lewis and Grotemut, *J. Am. Chem. Soc.*, 49, 1365 (1927).
[61] Harris and Frankforter, *J. Am. Chem. Soc.*, 48, 3144 (1926).
[62] Cox, *J. Am. Chem. Soc.*, 49, 1028 (1927).
[63] Nicolet and deMilt, *J. Am. Chem. Soc.*, 49, 1103 (1927).
[64] Berliner and May, *J. Am. Chem. Soc.*, 48, 2630 (1926); 49, 1007 (1927).
[65] May, Berliner and Lynch, *J. Am. Chem. Soc.*, 49, 1012 (1927).
[66] Klosky, Woo and Flanigan, *J. Am. Chem. Soc.*, 49, 1280 (1927).
[67] Smyth and Morgan, *J. Am. Chem. Soc.*, 49, 1030 (1927).
[68] Reiff, *J. Am. Chem. Soc.*, 48, 2893 (1926).
[69] Stephens, *J. Am. Chem. Soc.*, 48, 2920 (1926).

took place on the carbon atom attached to the ring and only if a hydrogen atom was attached directly to that carbon; the effect of water vapor on the ease of oxidation was studied. Adams, Cohen and Rees [70] have studied the most satisfactory conditions for the reduction of aromatic nitro compounds to aromatic amines by means of hydrogen and platinum-oxide platinum black, and Hiers and Adams [71] have used the same catalyst for the reduction of diphenylamine and triphenylamine to the corresponding completely hydrogenated compounds; Jordan [72] has reduced by means of nickel and hydrogen di-(4-hydroxy-3-methylphenyl)dimethyl methane to 4-hydroxy-3-methylcyclohexyl-4-hydroxy-3-methylphenyldimethyl methane and also to di-(4-hydroxy-3-methylcyclohexyl)dimethyl methane and di-(4-hydroxycyclohexyldimethyl) methane; Gibbs and Francis [73] have carried out the air or oxygen oxidation of isoborneol to camphor in the presence of vanadium oxide; Brown and Henke [74] the reduction with nickel and hydrogen in a solvent such as alcohol of azoxybenzene and azobenzene to hydrazobenzene; Downs [75] the oxidation of toluene to benzaldehyde by air over a catalyst using careful temperature control; Downs [76] has also described the purification of hydrocarbons by oxidation of impurities with air and a catalyst under carefully regulated conditions.

The work on free radicals at the University of Michigan is being continued and this year a paper by Lund [77] has described the preparation of various methoxy triaryl carbinols and their derivatives.

Raiford and Colbert [78] have studied the effect of substitution in the formation and reactivity of certain aromatic ethers. A large number of experiments on the condensation of aromatic nitro halogen compounds with aqueous alcoholic potassium hydroxide to give phenyl alkyl ethers and with phenols to give phenyl ethers are described. The splitting of the ethers and the bromination were also studied; Kirner [79] has compared the effect of the aromatic group on the activity of a halogen in different relative positions.

Erskine [80] has demonstrated the presence of aromatic hydrocar-

[70] Adams, Cohen and Rees, *J. Am. Chem. Soc.*, 49, 1093 (1927).
[71] Hiers and Adams, *J. Am. Chem. Soc.*, 49, 1099 (1927).
[72] Jordan, U. S. P. 1,593, 080 (July 20, 1926).
[73] Gibbs and Francis, U. S. P. 1,597,877 (Aug. 31, 1926).
[74] Brown and Henke, U. S. P. 1,589,936 (June 22, 1926).
[75] Downs, U. S. P. 1,589,632 (June 22, 1926).
[76] Downs, U. S. P. 1,590,965 (June 29, 1926).
[77] Lund, *J. Am. Chem. Soc.*, 49, 1346 (1927).
[78] Raiford and Colbert, *J. Am. Chem. Soc.*, 48, 2652 (1926).
[79] Kirner, *J. Am. Chem. Soc.*, 48, 2745 (1926).
[80] Erskine, *Ind. Eng. Chem.*, 18, 694, 722 (1926).

bons in gasoline and has worked out a determination of them; Catlin[81] has shown that cresylic acid is present in petroleum distillates. Crawford[82] has shown how to eliminate and rectify the phenol from crude ammonia liquors; Weber[83] has discussed antioxidants for rubber among which are certain aromatic compounds such as hydroquinone, *α*-naphthylamine, etc.; Ambler and Scanlan[84] have shown that naphthalene-1,6-disulfonic acid readily hydrolyzes to naphthalene; Rhodes and Eisenhauer[85] have determined the solubility of naphthalene in various aromatic hydrocarbons.

Tanner and Lasselle[86] have prepared very pure *o*-toluidine and have studied its properties in order to determine whether the presence of small amounts of *p*-toluidine which may occur in the commercial c.p. *o*-toluidine interferes with certain tests; Gibbs[87] has described a procedure for separating *p*-cresol quantitatively from *o*- and *m*-cresol.

Wheeler and Jennings[88] have described the dichloroacetic acid salts of various aromatic amines; Buehler and Heap[89] have compared the ease of formation of double salts of *m*-dinitrobenzene, *m*-dinitrotoluene, and *m*-dinitrophenol with aromatic amines and naphthalene.

Terry and Milas[90] have oxidized quinone or hydroquinone with sodium chlorate and osmium tetroxide and have isolated a new oxidation product which appears to be a dihydroxydihydroquinone.

Jackson[91] has added methyl hypobromite to benzalacetophenone and Worrall[92] has added aromatic amines to nitrostyrene to give *β*-substituted derivatives of phenylnitroethane.

In continuation of the work on ammono compounds, Strain[93] has shown the similarity in the reactions of hydrobenzamide and benzylidine amine with aromatic aldehydes thus demonstrating that these substances are ammono aldehydes.

Loh and Dehn[94] have studied the oxidation of thiocarbanilide and have obtained with various reagents diphenylurea. Nitric acid

[81] Catlin, *Ind. Eng. Chem.*, **18**, 743 (1926).
[82] Crawford, *Ind. Eng. Chem.*, **19**, 168 (1927).
[83] Weber, *Ind. Eng. Chem.*, **18**, 963 (1926).
[84] Ambler and Scanlan, *Ind. Eng. Chem.*, **19**, 417 (1927).
[85] Rhodes and Eisenhauer, *Ind. Eng. Chem.*, **19**, 414 (1927).
[86] Tanner and Lasselle, *J. Am. Chem. Soc.*, **48**, 2163 (1926).
[87] Gibbs, *J. Am. Chem. Soc.*, **49**, 839 (1927).
[88] Wheeler and Jennings, *J. Am. Chem. Soc.*, **49**, 1091 (1927).
[89] Buehler and Heap, *J. Am. Chem. Soc.*, **48**, 3168 (1926).
[90] Terry and Milas, *J. Am. Chem. Soc.*, **48**, 2647 (1926).
[91] Jackson, *J. Am. Chem. Soc.*, **48**, 2166 (1926).
[92] Worrall, *J. Am. Chem. Soc.*, **49**, 1598 (1927).
[93] Strain, *J. Am. Chem. Soc.*, **49**, 1558 (1927).
[94] Loh and Dehn, *J. Am. Chem. Soc.*, **48**, 2956 (1926).

gave aromatic nitro substitution as well. A number of complex salts of thiocarbanilide with metallic halides were described.

Kendall and Noyes[95] have prepared an optically active crystalline diazo compound by the action of sodium methylate upon the nitroso derivative of the anhydride of *cis*-aminocamphonanic acid. This is a continuation of the investigation to show that the two nitrogens in an aliphatic diazo compound are dissimilar and can cause asymmetry in the carbon to which they are attached.

Wheeler and Jennings[96] have made a further study of *p*-cymene derivatives; Hann and Spencer[97] have described the chlorination of vanillin; Gilbert[98] has prepared certain unsymmetrical benzoyl and substituted benzoylhydrazides and has studied their rearrangement products by heat. His conclusion is that the rearrangements take place around one of the nitrogen atoms in each case.

Conant and Pratt[99] have published a number of papers in their quantitative study of the oxidation and reduction of various organic compounds. The irreversible reduction of an organic compound may be formulated in electrochemical terms by determining the "apparent reduction potential," the normal potential of the reversible system that will just cause appreciable reduction (20-30% in 30 min.) under conditions specified; the A. R. P. can be determined if the action of the reagents is a function of the potential. The reduction of azo dyes has been described. The oxidation of phenols, amino phenols and enols with the various reagents of different potential has been carried out and the mechanism discussed. The free energy of reduction referred to the gaseous state of various quinones has been calculated from vapor pressure measurements of the quinones and hydroquinones and from the reduction potential referred to the solid state. The relation between structure and reduction potential is discussed.

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[95] Kendall and Noyes, *J. Am. Chem. Soc.*, **48**, 2404 (1926).

[96] Wheeler and Jennings, *J. Am. Chem. Soc.*, 49, 572 (1927).

[97] Hann and Spencer, *J. Am. Chem. Soc.*, **49**, 535 (1927).

[98] Gilbert, *J. Am. Chem. Soc.*, **49**, 286 (1927).

[99] Conant and Pratt, *J. Am. Chem. Soc.*, 48, 2468, 3178, 3220 (1926); 49, 293 (1927).

Chapter XXVII.

Heterocyclic Organic Chemistry.

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Very few outstanding accomplishments in research characterize the production in this field of chemistry this past year. As in the other branches of organic chemistry, the research work in heterocyclic chemistry has been influenced to a large degree by the demand for new products having medicinal value, and consequently emphasis has been laid chiefly on the practical features and the theoretical aspects of the subject have not received the attention that they should. Most of the publications are reports of short researches in limited fields. The various types of heterocyclic combinations which have been studied are the following: pyrimidines, purines and nucleosides, glyoxalines and thioglyoxalines, pyrroles, pyridines and piperidines, β- and γ-lactones, phenanthridones, thiazoles, isoxazolines and the acridines. No outstanding synthetic work dealing with the chemistry of the alkaloids, for example, has been contributed. The writer is looking forward to the time when this branch of heterocyclic chemistry will receive more attention in this country. We are not paying sufficient attention, as organic chemists, to the chemistry of plant products. Here is a rich field for scientific cultivation that we are neglecting, and which promises much for research workers trained in the technique of organic chemistry and biochemistry.

Those interested in the development of pyrimidine chemistry will appreciate the importance and simplicity of Davidson and Baudisch's[1] new method of synthesizing uracil. These workers have made use of a reaction first observed by von Pechmann,[2] who showed that malic acid undergoes decomposition when heated with strong sulfuric acid with formation of formylacetic acid. When this reaction is applied in the presence of an excess of urea uracil is produced in a yield of 50 — 55% of the theoretical. These same workers have also continued their study of the behavior of pyrimidines of the uracil type on oxidation.[3] They find that 5-aminouracil is oxidized by potassium ferricyanide with formation of diuracil-pyridazine. The reaction is expressed as follows:

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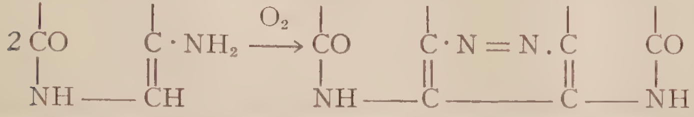
[1] *J. Am. Chem. Soc.,* 48, 2379 (1926).
[2] *Ber.,* 17, 929 (1884); *Ann.,* 264, 261 (1891).



The ionization of pyrimidines in relation to the structure of pyrimidine nucleosides, and the effect of ionization upon the optical properties of nucleic acid derivatives have been investigated by Levene and his co-workers, Bass and Simms.[4] They find that the dissociation constants of the nucleoside uridine and its derivatives do not furnish evidence which enables one to decide the structure of this nucleoside. The results, however, do not contradict the theory of the sugar union in position 3 of the pyrimidine. In the case of cytidine the dissociation constants are more significant and these workers conclude from their results that the pyrimidine-cytosine is proven by the evidence to be linked to sugar in position 3. Since cytidine can be converted into uridine the sugar linkage of the latter must be in the same position.

Further experimental evidence in support of the constitution of the nucleoside uridine has been obtained by Levene and Bass[5] in an investigation dealing with the action of hydrazine on this nucleoside. It has been shown that hydrazine and uracil interact to form urea and pyrazolone.[6] Thymine reacts in an analogous manner to form urea and 4-methylpyrazolone. When this reagent is allowed to interact with the nucleoside-uridine a ribose-free derivative of pyrazolone is obtained, but no perceptible quantities of urea could be isolated. They conclude from their experiments that no perceptible quantity of the sugar ribose is liberated from the uridine by the action of hydrazine, and that the isolation of ribose-free pyrazolone is an indication that in uridine the union of the sugar to uracil is in position 3 of the pyrimidine.

The only publication in the field of purines calling for consideration is one by Buell and Perkins[7] reporting the discovery of 2-oxy-6-aminopurine or oxyadenine in pig's blood. This may be regarded as an oxidation product of adenine.

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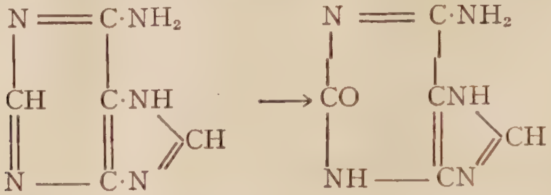
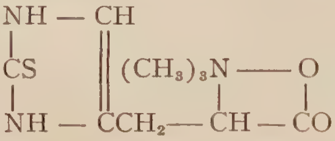
[3] *J. Biol. Chem.*, 71, 497 (1926).
[4] *J. Biol. Chem.*, 70, 229, 243 (1926).
[5] *J. Biol. Chem.*, 71, 167 (1926).
[6] Fosse, Hieulle and Bass, *Compt. rend.*, 178, 811 (1924).



The outstanding development this past year in the field of glyoxaline chemistry was the discovery, independently, by Eagles and Johnson,[8] and Newton, Benedict and Dakin[9] that the organic sulfur compound discovered in pig's blood by Bulmer, Eagles and Hunter,[10] and Benedict, Newton and Behre[11] is identical with ergothioneine first discovered in ergot of rye by Tanret,[12] and whose constitution is to be represented structurally as the betaine derivative of thiol-histidine.[13]



In the light of these results, and in order to avoid confusion in nomenclature, it is now in order to discontinue the usage of the names sympectothion[14] and thiazine[9] assigned to this sulfur constituent of blood, and to adopt the name—*ergothioneine*—originally proposed by its discoverer, Tanret. The discovery of this new type of sulfur compound in the animal organism has stimulated a renewed interest in the biochemistry of the element sulfur.

Any analytical procedure that will enable biochemists to make more accurate determinations of histidine and arginine is worthy of special consideration. Two papers of importance in this field have been contributed by Vickery[15] and Vickery and Leavenworth.[16] Vickery finds that histidine is precipitated quantitatively in pure form as the di-salt of 2,4-dinitro-1-naphthol-7-sulfonic acid from a solution containing excess of this sulfonic acid reagent. This salt presents many advantages over other salts of histidine which have been described not only for isolation but for the purification of histidine. Vickery and Leavenworth have improved on Kossel's method of separating histidine from arginine by means of their silver salts. They find that histidine can be completely separated from arginine by bringing the reaction of a solution of the two bases, which also contain an excess of a soluble silver salt, to pH 7.0. By a second precipitation as silver compound a histidine fraction is obtained containing no material quantity of arginine. No appreciable amount of histidine escapes precipitation, the arginine fraction being free from this base. Arginine silver is subsequently precipitated at a strong alkaline reaction of pH 10 to 11.

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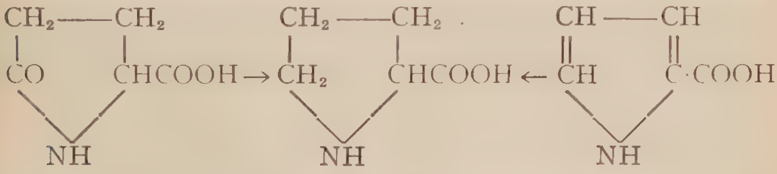
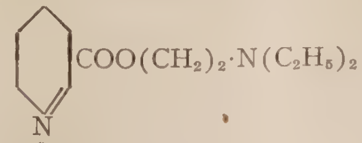
[7] *J. Biol. Chem.*, 72, 745 (1927).
[8] *J. Am. Chem. Soc.*, 49, 575 (1927).
[9] *Science*, 64, 602 (1926); *J. Biol. Chem.*, 72, 367 (1927).
[10] *J. Biol. Chem.*, 63, 17 (1925); 65, 623 (1925).
[11] *J. Biol. Chem.*, 64, 215 (1925); 67, 267 (1926).
[12] *J. pharm. chim.*, (VI), 30, 145 (1909).
[13] Barger and Ewins, *J. Chem. Soc.*, 99, 2336 (1911).
[14] Hunter and Eagles, *J. Biol. Chem.*, 72, 123 (1927).
[15] *J. Biol. Chem.*, 71, 303 (1926).
[16] *J. Biol. Chem.*, 72, 403 (1926).

The only publication in the field of pyrrole chemistry is one by McCay and Schmidt,[17] in which they describe the results of unsuccessful experiments undertaken to develop a satisfactory synthesis of the aminoacid proline. They were unable to reduce pyrrolidone-α-carboxylic acid or pyrrole-α-carboxylic acid to proline.



In order to obtain new local anesthetics having the properties of procaine, Ingersoll and Robbins [18] have synthesized two esters of the procaine type derived from nicotinic acid, namely: the diethyl aminoethyl- and diethyl aminopropyl-derivatives. Pharmacological tests revealed the surprising fact that both of these combinations are devoid of local anesthetic action.



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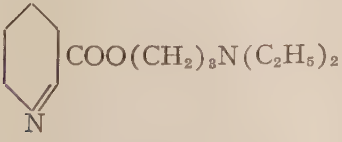

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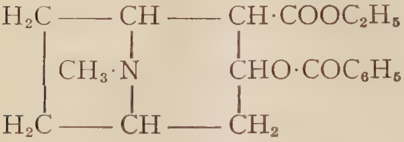
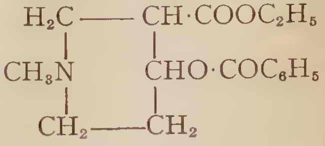
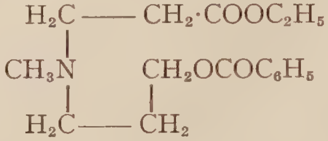
[17] *J. Am. Chem. Soc.*, 48, 1933 (1926).
[18] *J. Am. Chem. Soc.*, 48, 2449 (1926).

New local anesthetics of high potency have been discovered by McElvain[19] in his researches on new derivatives of piperidine. The cyclic compounds which he has prepared are closely related in structure to cocaine, and as long as the cyclic structure is preserved local anesthetic properties are maintained.[20] The general method of synthesis which he utilizes for the preparation of his new combinations is based on the molecular condensation of esters of iminopropionic acid by interaction with sodium, followed by reduction to the required alcohol. The steps of this synthesis are represented below:


(Cocaine)


(Very active)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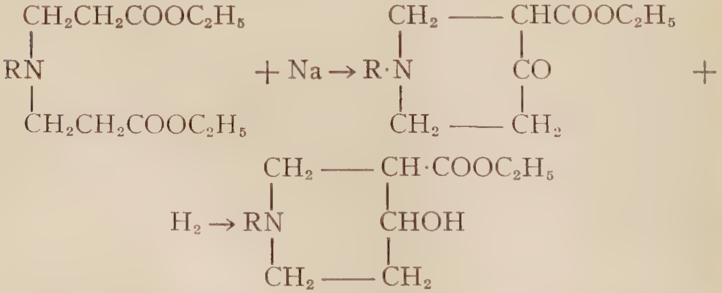

McElvain has studied the effect of changing the alkyl groups (R) attached to nitrogen in his cycles[19] and, as a result, has made some very interesting observations. The different alkyl groups studied were—ethyl, *n*-propyl, iso-propyl, *n*-, iso- and sec-butyl, and *n*- and iso-amyl. The most striking feature of the research is the marked decrease in toxicity as the size of the alkyl group attached to nitrogen is increased. Anesthetic action increases with size of the alkyl group. The amyl compound was found to be 20% as toxic as procaine, and showed one-thirtieth of the toxicity of cocaine. The anesthetic power of the amyl compound is considerably greater than that of cocaine.

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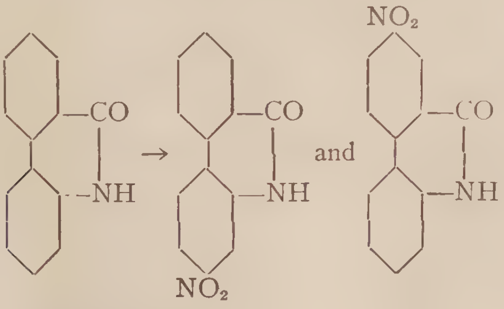
[19] *J. Am. Chem. Soc.,* **48**, 2179 (1926).
[20] *J. Am. Chem. Soc.,* **46**, 1721 (1924).

In his last paper McElvain[21] describes the preparation of cycles containing the group *p*-aminobenzoyl in place of the benzoyl radical, but finds that such combinations are more toxic than the corresponding benzoates. Furthermore, increase in size of the side chain R attached to nitrogen caused an increase in the duration of anesthesia and decrease in toxicity.

Dox[22] finds that six and seven membered hydrazolactones containing two nitrogens and one oxygen can be prepared easily from *β*-chlorethyl and *γ*-chlorpropyl esters of phenylcarbazic acid. These represent new types of combinations. They show no noteworthy pharmacological activity.

The ring system phenanthridone has been very little studied. Moore and Huntress[23] have contributed to the chemistry of this compound by describing methods of synthesizing the 2-nitro and 7-nitro derivatives of this ring. These have been prepared from 4-nitrodiphenic anhydride by way of two isomeric 4-nitrodiphenamic acids.



(Phenanthridone)

Bogert and Allen, and Bogert and Updike[24] have contributed two papers on thiazoles. Five new isomers of dehydrothio-*p*-toluidine carrying their methyl and amino groups in other positions have been synthesized. In their last paper Bogert and Updike have extended our knowledge of this series by preparing several new benzothiazoles through condensation of the monothiosulfuric acid of *p*-amino-dimethylaniline with the nitrobenzaldehydes and the hydroxybenzaldehydes.

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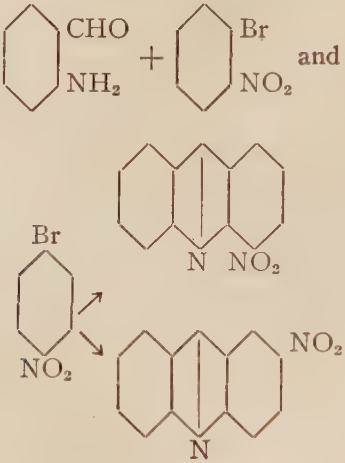
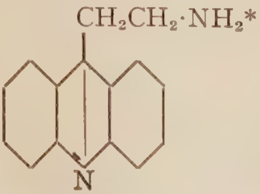
[21] *J. Am. Chem. Soc.*, 48, 2239 (1926).
[22] *J. Am. Chem. Soc.*, 48, 1951 (1926).
[23] *J. Am. Chem. Soc.*, 49, 1324 (1927).
[24] *J. Am. Chem. Soc.*, 49, 1315 (1927); 49, 1373 (1927).

Jensen and Friedrich[25] have been able to show that the two nitro derivatives formed by nitration of acridine are 1(9)- and 3(7)-nitroacridines. Their structures have been established by synthesis. This is easily accomplished by condensation of *o*-aminobenzaldehyde with *o*-nitrobromo- and *p*-nitrobromobenzene, respectively.



Jensen and Howland[26] have also prepared for pharmacological study acridine-5-ethylamine.



The authors state that further experiments in the preparation of the corresponding amino- and methylamino-acridines are in progress in order that their physiological effects may be studied.

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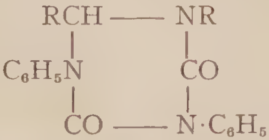
[25] *J. Am. Chem. Soc.*, **49**, 1049 (1927).

[26] *J. Am. Chem. Soc.*, **48**, 1988 (1926).

* In the original paper this amine is incorrectly described as acridine-9-ethylamine.

Kohler has continued his studies on isoxazoline oxides and has contributed two papers.[27] The paper with Goodwin is really a correction of the paper with Shohan in which the reactions studied were incorrectly formulated.

The last paper to be referred to in this report is one by Lange.[28] He finds that nitrogen-alkyl and nitrogen-aryl Schiff bases can be distinguished by their behavior towards phenylisocyanate. The alkyl substituted amines interact with phenylisocyanate in a similar manner as isocyanic acid giving 6-membered diketocyanidines. All attempts to obtain addition compounds with phenylisocyanate and aryl substituted amines were unsuccessful. Phenylisocyanate does not add to the CH = N linking in hydrazones.



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[27] Kohler and Shohan, *J. Am. Chem. Soc.*, 48, 2425 (1926); Kohler and Goodwin, *J. Am. Chem. Soc.*, 49, 219 (1927).

[28] *J. Am. Chem. Soc.*, 48, 2440 (1926).

Chapter XXVIII.

Metallo-Organic Compounds I.

ELEMENTS OF THE SECOND GROUP.

Frank C. Whitmore,
Northwestern University

The American publications of the year have been very meagre except as regards reactions and uses of the Grignard reagent.

Kharasch and Marker[1] have determined the relative electronegativity of some seventeen organic residues by studying the products of the action of hydrochloric acid on a large number of mixed organic mercury compounds of the type, RHgR′, prepared by means of the Grignard reagent. The line of reasoning may be illustrated by an example. Phenyl mercury naphthyl reacts with hydrochloric acid to give only phenylmercuric chloride and naphthalene. Thus the naphthyl radical is concluded to be more electronegative than phenyl.

Hager and Marvel[2] have utilized mercury alkyls and lithium alkyls in attempting to prepare compounds having five alkyl radicals attached to a nitrogen atom. They have developed a very satisfactory method for preparing pure lithium alkyls.

Richards, King and Hall[3] have painstakingly tested the possibility of separating lead into its isotopes by the disproportionation of lead diphenyl into metallic lead and lead tetraphenyl. No separation was obtained. King[4] has made similar futile attempts to separate isotopes of mercury by disproportionation reactions, two of which involve metallo-organic compounds. He treated mercurous chloride with ethylmagnesium bromide to form metallic mercury and mercury diethyl. He also treated phenylmercuric acetate with sodium stannite to give metallic mercury and mercury diphenyl. An intermediate organic "mercurous" compound is assumed.

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[1] *J. Am. Chem. Soc.*, **48**, 3130 (1926).
[2] *J. Am. Chem. Soc.*, **48**, 2689 (1926).
[3] *J. Am. Chem. Soc.*, **48**, 1530 (1926).
[4] *J. Am. Chem. Soc.*, **49**, 1500 (1927).

Fuson[5] has completed very careful studies on the action of the Grignard reagent with organic halides and has shown the earlier work on this subject to be at fault. Benzyl halides with methylmagnesium iodide yield ethylbenzene, ethane and dibenzyl. About 65% of the materials used appear as the last two substances. The by-product which was mistaken by Späth for 1,2,3-triphenylpropane is really *p*-benzyldibenzyl formed from dibenzyl and benzyl halide during the purification of the product.

Gomberg and Bachmann[6] have studied the reducing action of a mixture of magnesium iodide and magnesium on ketones and have concluded that the reducing agent is magnesium monoiodide. They have also studied the "activating" action of iodine in preparing the Grignard reagent. Gilman and Adams[7] have confirmed the work of Gilman and Pickens[8] on the mechanism of the reduction of azobenzene by the Grignard reagent. The reaction takes place through an intermediate product which has a MgX group attached to each nitrogen atom. Gilman and Morris[9] have shown that the Grignard reagent adds to the terminal double bond in thionylanilines. Gilman and McCracken[10] have found that nitrosobenzene reacts with phenylmagnesium iodide to form mainly diphenyl and diphenylamine. Gilman, Robinson and Beaber[11] have studied the action of the Grignard reagent with esters of sulfuric, sulfenic, thiocarboxylic, thioncarboxylic and dithiocarboxylic acids without detecting any alkylating action such as is shown by esters of many sulfonic acids.

Hurd and Webb[12] have prepared Grignard reagents from diarylvinyl bromides by means of the magnesium copper alloy recommended by Gilman. Gilman and Kirby[13] have succeeded in obtaining small yields of benzhydrylmagnesium chloride. With methyl sulfate it gives *unsym.*-diphenylethane.

The Grignard reagent has been used by Conant, Small and Sloan[14] in preparing various complex dixanthyls used in further studies of free radicals. Tomecko and Adams[15] have used the Grignard reaction to prepare 9-, 10-, 11-, 12- and 13-hydroxystearic acids. Hiers and Adams[16] have used the Grignard reagent extensively in the synthesis of ω-cyclohexyl aliphatic acids. McCay and Schmidt[17] have used the Grignard reagent in preparing pyrrole-α-carboxylic acid. Indications are obtained that pyrrylmagnesium iodide has the magnesium attached to nitrogen.

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[5] *J. Am. Chem. Soc.*, 48, 2681, 2937 (1926).
[6] *J. Am. Chem. Soc.*, 49, 236 (1927).
[7] *J. Am. Chem. Soc.*, 48, 2004 (1926).
[8] *J. Am. Chem. Soc.*, 47, 2406 (1925).
[9] *J. Am. Chem. Soc.*, 48, 2399 (1926).
[10] *J. Am. Chem. Soc.*, 49, 1052 (1927).
[11] *J. Am. Chem. Soc.*, 48, 2715 (1926).
[12] *J. Am. Chem. Soc.*, 49, 546 (1927).
[13] *J. Am. Chem. Soc.*, 48, 1733 (1926).
[14] *J. Am. Chem. Soc.*, 48, 1743 (1926).

Gilman and Meyers[18] have made further studies on the methods of determining the Grignard reagent. Gaddum and French[19] have studied the electrolysis of Grignard solutions.

Gilman and Schulze[20] have prepared a number of cyanocalcium iodides in poor yields. They appear to offer no advantages in synthetic work.

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[15] *J. Am. Chem. Soc.*, **49**, 522 (1927).
[16] *J. Am. Chem. Soc.*, **48**, 2385 (1926).
[17] *J. Am. Chem. Soc.*, **48**, 1933 (1926).
[18] *Rec. trav. chim.*, **45**, 314 (1926).
[19] *J. Am. Chem. Soc.*, **49**, 1295 (1927).
[20] *J. Am. Chem. Soc.*, **48**, 2463 (1926).

Chapter XXIX.

Metallo-Organic Compounds II.

ELEMENTS OF THE FOURTH GROUP.

Charles A. Kraus,
Brown University

The term "metallo-organic" is applied to various compounds of the metallic elements with organic groups. Excepting the organic derivatives of the more electropositive elements, such as the alkali metals, the metallo-organic compounds do not differ essentially from corresponding derivatives of the non-metallic elements; in the metallo-organic compounds, the metallic elements function in their non-metallic capacity. In the case of hydrocarbon derivatives of non-metallic or metallic elements of lower valence, the reactions of the compounds in question usually involve the reaction of various organic groups along with that of the inorganic atom. In the case of elements of higher valence, and this is particularly true of the elements of the fourth group, the metallo-organic compounds enter into many reactions in which the organic groups do not function at all, the reaction being confined to the atom of the inorganic element. It is in these compounds that inorganic and organic chemistry overlap. A study of the metallo-organic compounds, therefore, is equally important to inorganic and to organic chemistry.

While the chemistry of metallo-organic compounds was actively cultivated for a quarter of a century immediately following their discovery about 1850, the subject was subsequently neglected by both organic and inorganic chemists. More recently mercury and the elements of the fifth group have been investigated rather extensively with a view to their utilization in pharmaceutical preparations, but the elements of the fourth group, as well as other metallic elements, have for years received little systematic attention. Probably few chemists realize how extensive is the chemistry of the elements lead, tin, germanium, silicon and boron. Stock's preparation of an extended series of hydrides of boron[1] and silicon[2] and Dennis's recent preparation of several of the simpler hydrides of germanium,[3] point unmistakably toward an extensive and varied chemistry of these elements.

The tardy development of the chemistry of the elements of the fourth group, aside from carbon, is in no small measure due to lack of suitable synthetic reagents. Most of the reagents hitherto used for this purpose are such as are commonly employed in the synthesis of carbon compounds and are by no means adapted to the new requirements imposed by such elements as silicon, germanium and tin. The most promising reagents for use in connection with the metallo-organic derivatives of the elements of the fourth group are compounds of the type Na_nMR_{4-n} where Na represents sodium or an alkali metal, M an element of the fourth group, such as tin, germanium or silicon, and R a univalent organic group or hydrogen. Compounds of the type $NaSnR_3$ have recently been employed by Kraus and Sessions[4] in the preparation of a number of new organic tin derivatives, while compounds of the type Na_2SnR_2 have been employed by Kraus and Greer[5] for various preparations, including the synthesis of chains of saturated tin atoms up to the stannopentane, Sn_5R_{12}.

Compounds of the type Na_3SnR have not as yet been investigated, but it is of interest to point out that compounds of the type Na_4M are representatives of a familiar series of intermetallic compounds whose properties present many points of interest.[6]

Compounds of the type $NaMR_3$ are close analogues of sodium methyl, $NaCH_3$, and corresponding derivatives of other alkyl and aryl groups. Such compounds have been prepared by Schlenk[7] and some of their properties have been studied by various investigators.[8] It is generally conceded that the alkali metal alkyls are of the nature of salts, whose properties are closely analogous to those of the corresponding hydrides. Because of their extreme reactivity and the somewhat round-about method by which they are prepared, they have not as yet been studied extensively by organic chemists with a view to their utilization as synthetic reagents. It is scarcely to be doubted, however, that these compounds would prove to be ideally adapted to carrying out the synthesis of some of the more complex hydrocarbons.

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[1] Stock and Pohland, *Ber.*, 59, 2210, 2215, 2223 (1926); Stock, *Ber.*, 59, 2226 (1926).

[2] Stock, *Z. Electrochem.*, 32, 341 (1926).

[3] Dennis, Corey and Moore, *J. Am. Chem. Soc.*, 46, 657 (1924).

[4] *J. Am. Chem. Soc.*, 47, 2361 (1925).

[5] *J. Am. Chem. Soc.*, 47, 2568 (1925).

[6] Kraus, *J. Am. Chem. Soc.*, 44, 1216 (1922).

[7] Schlenk and Holtz, *Ber.*, 50, 262 (1917).

[8] Hein and Segitz, *Z. anorg. allgem. Chem.*, 158, 153 (1926).

An alkyl or aryl group is moderately electropositive and rather weakly electronegative so that the sodium salts of these radicals are highly reactive towards hydrolyzing and oxidizing agents. In the presence of strongly, or moderately strongly, electronegative elements, or compounds containing such elements, the electron, rather loosely held on the metallo-organic radical, tends to combine with the more strongly electronegative element. It is this property that makes these compounds valuable as synthetic reagents.

Triphenylmethyl, and other triaryl methyls, behave as though they were markedly more electronegative than methyl or other similar simple organic radicals. Reaction between the alkali metals and triphenylmethyl, therefore, takes place readily and the resulting salt, sodium triphenylmethyl, is moderately stable toward oxidizing and hydrolyzing agents. Thus, as Kraus and Rosen [9] have shown, potassium triphenylmethyl is not ammonolyzed in liquid ammonia solution.

While the properties characteristic of the triphenylmethyl group appear only in compounds of the type R_3C, in which the substituents R are aryl groups, in the case of the elements silicon, germanium and tin, groups of the type MR_3 exhibit properties closely analogous to those of triphenylmethyl, regardless of the nature of the substituent groups R, which may in fact be alkyl or aryl groups or hydrogen. Thus, in the case of tin, there have been obtained the compounds $NaSn(CH_3)_3$ and $NaSn(C_6H_5)_3$, which resemble each other closely in physical, as well as chemical properties. In the case of germanium, we have not only such compounds as $NaGe(C_6H_5)_3$, but also $NaGeH_3$,[10] which latter compound is the germanium analogue of sodium methyl, $NaCH_3$. While, in the case of carbon, the properties of groups of the type CR_3 are greatly modified, depending upon whether the substituents R are aryl or alkyl groups or hydrogen, in the case of the corresponding derivatives of other elements of the fourth group, corresponding to the type MR_3, the nature of the substituents R has little influence on the properties of the resulting compound.

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[9] *J. Am. Chem. Soc.*, 47, 2739 (1925).

[10] Unpublished observations by E. Seaton Carney, Chemical Laboratory, Brown University.

Compounds of the type $NaMR_3$ are salts in the true sense of the word. They are readily soluble in liquid ammonia and, curiously enough, certain of them are soluble in organic solvents, such as ether or even benzene. Their solutions in liquid ammonia are highly ionized and relatively stable. The liquid ammonia solutions constitute ideal reagents for the preparation of various derivatives of the elements silicon, germanium and tin, and the reactions involved are in many cases instantaneous and quantitative. At the present time, these compounds are, therefore, the most promising reagents we have for the purpose of synthesizing the more complex derivatives of the elements of the fourth group.

The use of compounds of the type Na_2MR_2 has not been as extensively developed as has that of the simpler derivatives $NaMR_3$. There is good reason for believing that the former compounds will prove as readily applicable as the latter, and that, in some respects, they will prove of even greater importance.

Having discussed some of the more general aspects of the problems relating to metallo-organic compounds, we may turn to a consideration of the detailed investigations that have appeared during the past year.

Germanium. The work of Dennis and his collaborators on the preparation of organic derivatives of germanium was reviewed in volume I of this Survey. During the present year there has appeared a paper by Kraus and Foster [11] in which the work with organic germanium compounds has been extended. Their investigation was confined chiefly to derivatives of the triphenyl germanium radical. They give detailed directions for the preparation of tetraphenyl germanium and triphenyl germanium bromide which served as source materials for further preparations. The real starting point of their investigation was sodium triphenyl germanyl, $NaGe(C_6H_5)_3$, which was prepared by the direct action of sodium on triphenyl germanium, the latter compound having been prepared according to the method of Morgan and Drew.[12] Sodium triphenyl germanyl is a salt which is readily soluble in liquid ammonia with a faint yellow color. It is also soluble in benzene, particularly in the presence of ammonia vapors. Since sodium triphenyl germanyl is a salt, the electron due to sodium is evidently attached to the triphenyl germanium radical forming therewith the anion, $(C_6H_5)_3Ge^-$. This anion is sufficiently electronegative so that it does not ammonolyze in liquid ammonia solution. On the other hand, in the presence of more strongly electronegative elements, whether combined or uncombined, it tends to react with loss of its electron. On treating sodium triphenyl germanyl with ammonium bromide, triphenyl germane is formed according to the reaction:

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[11] *J. Am. Chem. Soc.*, **49**, 457 (1927).
[12] *J. Chem. Soc.*, **127**, 1760 (1925).

$$NaGe(C_6H_5)_3 + NH_4Br = NaBr + (C_6H_5)_3GeH + NH_3.$$

Triphenyl germane melts at 47°, and a less stable form at 27°. Sodium triphenyl germanyl reacts directly with molecular oxygen in liquid ammonia solution with the formation of sodium triphenyl germanolate, $(C_6H_5)_3GeONa$, which, on hydrolysis, yields the germanol, $(C_6H_5)_3GeOH$, M.P. 134.2°.

Sodium triphenyl germanyl reacts with trimethyl tin bromide according to the equation:

$$NaGe(C_6H_5)_3 + (CH_3)_3SnBr = NaBr + (C_6H_5)_3Ge\,Sn(CH_3)_3.$$

The compound so formed is a mixed stanno-germano-ethane, or trimethyl stannyl triphenyl germane, M.P. 88°. It is comparatively stable. Kraus and Foster also prepared triphenyl germanium fluoride, M.P. 76.6°, and triphenyl germanium iodide, M.P. 157°.

Tin. Kraus and Bullard[13] have further studied the trimethyl tin radical. For this purpose they have, in general, made use of sodium trimethyl stannyl in liquid ammonia as reagent. Kraus and Sessions[4] have shown that in boiling benzene, trimethyl tin or hexamethyl stannoethane is largely dissociated into the free group, the extent of dissociation depending on the concentration. According to Kraus and Bullard, the same compound in benzene near its freezing point is completely polymerized to the stannoethane, even at relatively low concentrations. They have also studied the compound formed between the trimethyl tin and triethyl tin radicals. They have shown that the products formed according to the reactions:

$$NaSnR'_3 + R''_3SnBr = NaBr + R'_3Sn\cdot SnR''_3, \qquad (1)$$

and

$$NaSnR''_3 + R'_3SnBr = NaBr + R''_3Sn\cdot SnR'_3, \qquad (2)$$

in liquid ammonia solution, are apparently identical compounds involving the groups R'_3Sn and R''_3Sn. With R′ and R″ methyl and ethyl groups respectively, a liquid was obtained which failed to freeze at temperatures as low as — 50°. That it was not a mixture of hexamethyl stannoethane and hexaethyl stannoethane, was shown by studying mixtures of these compounds. In the latter case, hexamethyl stannoethane separated out at temperatures only slightly below 0°. With $R' = $ methyl and $R'' = $ phenyl, a compound was obtained melting at 106°, whose properties corresponded to those of the compound $(C_6H_5)_3Sn{\cdot}Sn(CH_3)_3$. It should be pointed out that, in this case, the products obtained according to reactions (1) and (2) were identical except that reaction (2) did not proceed quantitatively.

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[13] *J. Am. Chem. Soc.,* 48, 2131 (1926).

The same authors prepared trimethylbenzyl tin which boils in the neighborhood of 215°. On brominating this compound, the benzyl group is substituted.

Bullard and Robinson[14] have prepared the mixed methylphenyl stannanes corresponding to the general formula $(C_6H_5)_nSn(CH_3)_{4-n}$. Methyltriphenyl stannane, melting at 60-61°, was prepared by treating sodium triphenyl stannyl with methyl iodide in liquid ammonia solution with a yield of 90%. Dimethyldiphenyl stannane was prepared by treating disodium diphenyl stannide with methyl iodide in liquid ammonia with a yield of 84%. It distils with decomposition at 127-140° at a pressure of 3 mm. The converse reaction, in which disodium dimethyl stannide was treated with phenyl iodide, did not lead to the desired result. Attempts to prepare trimethylphenyl stannane by treating sodium trimethyl stannide with phenyl bromide in liquid ammonia resulted in a mixture which appeared to consist chiefly of the desired stannane, $(CH_3)_3SnC_6H_5$, with a smaller quantity of tri-trimethyl stannyl amine, $[(CH_3)_3]_3N$, and benzene. This stannane was also prepared by means of the Grignard reagent. On brominating the mixed phenylmethyl stannanes in various solvents, phenyl groups were substituted.

Lead. Browne and Reid[15] have prepared a number of derivatives of triethyl lead, chiefly through the action of the acids on tetraethyl lead. This reaction was facilitated by the presence of silica gel. They give directions for the preparation of triethyl lead chloride and triethyl lead hydroxide as well as of triethyl lead acetate. Attempts to prepare the triethyl lead derivatives of various weak inorganic acids through metathetic reaction with triethyl lead acetate were, in general, unsuccessful. The triethyl lead salts of the following fatty acids were prepared and the melting points determined: propionate (141-142°), isobutyrate (119.4-121.8°), valerate (115.6-117.0°), isovalerate (119.4-119.8°), caproate (94.7-95.8°), heptoate (90.0-90.8°), caprylate (85.0-87.5°), pelargonate (88.0-90.0°). The following salts of halogenated acetic acids were likewise prepared: chloroacetate (146-146.5°), dichloroacetate (113.5-114.5°), trichloroacetate (135.5-138.6°), bromoacetate (121°), dibromoacetate (98.6-101.8°). Many of these salts become unstable as the melting point is approached.

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[14] *J. Am. Chem. Soc.*, 49, 1368 (1927).

[15] *J. Am. Chem. Soc.*, 49, 830 (1927).

Chapter XXX.

Metallo-Organic Compounds III.

ELEMENTS OF THE FIFTH GROUP.

Cliff S. Hamilton,
Northwestern University

Some metallo-organic compounds of the members of the fifth group of elements are known to possess considerable medicinal value. It is not surprising, therefore, that many of the articles on arsenic, antimony and bismuth, appearing in American scientific journals during the past year, deal with their clinical use. Of the published investigations but few have been of a purely chemical nature.

A very excellent piece of work by Loevenhart and Stratman-Thomas[1] deals with the relation of chemical constitution of arsenicals to their activity in neurosyphilis and trypanosomiasis. Special reference has been given to tryparsamide, $NaHO_3AsC_6H_4NHCH_2CONH_2$. These investigators have reached the conclusion that the action of tryparsamide in trypanosomiasis cannot be attributed to "any inherent chemical potentiality" of the $—CONH_2$ group; that the function of the NH_2 group is to block the carboxyl group; and that the presence of the methylene group in the side chain attached to the amino-nitrogen is essential in tryparsamide. They have found no other drugs as effective in paresis, and have come to the conclusion that the effect of tryparsamide in paresis is due to certain unknown physical or chemical properties of the drug.

Palmer and Edee[2] have made a study of aliphatic-aromatic arseno compounds. They point out that in the preparation of aryl arsenoacetic acids precautions are necessary, which are not usually required in the preparation of arseno compounds. These workers have synthesized members of the previously unknown series of unsymmetrical tetraarseno compounds and have also prepared the first hexaarseno compound of the aliphatic-aromatic type.

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[1] *J. Pharmacol.*, 29, 69 (1926).
[2] *J. Am. Chem. Soc.*, 49, 998 (1927).

A study of 2,3-dicarboxyphenylarsonic acid and its anhydride has been published by Hamilton and Frazier.[3] This should shortly lead to the preparation of arsonated phthaleins, related to phenolphthalein, fluorescein, and eosin.

In the field of heterocyclic arsenicals, Gottlieb-Billroth [4] has investigated dibenzoarsenole. He has prepared a number of derivatives of the parent compound, all of which contain arsenic as a member of an unsaturated five-membered ring.

A review of the literature dealing with organic compounds containing antimony indicates that little is being done in this field. Dunning and Reid [5] have synthesized some azo dyes containing antimony. These have been prepared by diazotizing stibanilic acid and then coupling with various substituted phenols. The acids form disodium salts which are water soluble thus making them available for therapeutic study. The results of the study of the pharmacology of these dyes have not been reported.

The work on bismuth compounds is limited for the most part to a chemical study of organic bismuth salts, such as the tartrates, etc. Harden and Dunning [6] report the preparation of bismuth thioglycolamide as a pure crystalline product. The pharmacological action of the compound is being investigated.

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[3] *J. Am. Chem. Soc.*, 48, 2414 (1926).
[4] *J. Am. Chem. Soc.*, 49, 482 (1927).
[5] *J. Am. Chem. Soc.*, 48, 2959 (1927).
[6] *J. Am. Chem. Soc.*, 49, 1017 (1927).

Chapter XXXI.

Sugar Chemistry.

Claude S. Hudson,

Chemist, National Bureau of Standards

The Occurrence and Preparation of Sugars. The pectic acid which is obtained from orange pectin by Wichmann and Chernoff's method for determining pectin in fruit products has been shown by Nelson[1] to be identical with the substance which Ehrlich and Sommerfield have recently isolated from the pectin of the sugar beet and shown to be a di-galacturonic acid, best characterized by its crystalline cinchonine salt.

The large scale production of crystalline glucose from the acid hydrolysis of starch gives a yield which, though remunerative, is much below theory. The identification of pure saccharine components of the by-product sirup is a problem of much scientific interest as well as of possible importance to the industry. The first step in this field has been made by Berlin[2] through his isolation of a small proportion of gentiobiose (as its crystalline β-octaacetate) from the sirup.

Continuing the researches on the composition of mesquite gum which have already shown it to be the best source for the preparation of *l*-arabinose, Anderson and Sands[3] have now isolated *d*-galactose as one of its constituents and they report that acid hydrolysis yields from it about 51% arabinose, 19% galactose, 13% of an aldehyde acid belonging to the glucuronic acid group, and only small amounts of mineral matter and nitrogenous material.

Spanish moss has been found to contain, as carbohydrate constituents, galactan, araban, xylan, cellulose, and an amorphous substance which appears to be a phenol methyl ether glucoside.[4]

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[1] Nelson, *J. Am. Chem. Soc.*, 48, 2412 (1926).
[2] Berlin, *J. Am. Chem. Soc.*, 48, 2627 (1926).
[3] Anderson and Sands, *J. Am. Chem. Soc.*, 48, 3172 (1926).
[4] Schorger, *Ind. Eng. Chem.*, 19, 409 (1927).

Articles relating in part to the preparation of monobenzoylglucuronic acid, talonic acid, neolactose, celtrobiose, 4-glucosidomannose, and hexonic and bionic acids are mentioned later.

Hydrolysis of Sugars. The measurement of single-ion activities in solutions containing sucrose and hydrochloric acid by electromotive force determinations has been shown by Scatchard [5] to be very uncertain because the electrode potentials change during inversion of the sugar and the liquid-junction potential appears to be altered by sucrose. His critical recalculation [6] of the rates of inversion of sucrose recently published by Pennycuick [7] lead him to conclude that the reaction is unimolecular within a few parts per thousand.

Nelson and Anderson [8] find that the retardation of the action of invertase on sucrose by the α- and β-forms of glucose and fructose is a function of the sucrose concentration and it may be doubted whether the theoretical views on the mechanism of invertase activity which have been developed by some investigators on the basis of these retardations have good foundation. Whether the hydrolysis of sucrose by invertase should be considered as proceeding in a heterogeneous or homogeneous medium is discussed by Nelson and Larson [9] from Michaelis and Menten's data, and it is concluded that the question is still an open one, although the great retardation of the rate in higher sucrose concentrations indicates that selective adsorption displacements play a role of the type observed in the adsorption of acetic acid from its mixtures with water by charcoal and that therefore the reaction is in a heterogeneous medium. If such is the case the mass law expressions of Michaelis and Menten lose most of their theoretical significance and the complex kinetic data of invertase action must be reinterpreted from the standpoint of adsorption phenomena. The point at issue here involves a matter that has been discussed by Hitchcock,[10] who shows that under some experimental conditions there is a formal identity of adsorption isotherm equations with the law of mass action.

Paine and Balch [11] report a precision measurement of the Clerget constant for the hydrolysis of sucrose and raffinose by invertase. The use of invertase in the preparation of sugar cane sirup of sufficiently high density to prevent fermentation, which was introduced some years ago by Dale and Hudson, has now been extended along the same lines by Paine and his associates[12] to prevent the bursting fermentation of chocolate-coated fondant candy. The critical solids content was found to be about 79% and fondants containing a sirup phase of higher strength were practically free from yeast fermentations.

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[5] Scatchard, *J. Am. Chem. Soc.*, 48, 2026 (1926).
[6] Scatchard, *J. Am. Chem. Soc.*, 48, 2259 (1926).
[7] Pennycuick, *J. Am. Chem. Soc.*, 48, 6 (1926).
[8] Nelson and Anderson, *J. Biol. Chem.*, 69, 443 (1926).
[9] Nelson and Larson, *J. Biol. Chem.*, 73, 223 (1927).
[10] Hitchcock, *J. Am. Chem. Soc.*, 48, 2870 (1926).
[11] Paine and Balch, *J. Am. Chem. Soc.*, 49, 1019 (1927).

The Oxidation of Sugars. A method for the preparation of hexonic and bionic acids which makes use of barium hypoiodite as the oxidant and gives high yields has been perfected by Goebel.[13]

Valuable experimental and theoretical contributions to the knowledge of the behavior of sugars in alkaline solutions have been made by Evans and associates.[14] In the first article the yields of formic, acetic and lactic acids, pyruvic aldehyde and galacto-metasaccharinic acid were measured as functions of temperature and alkalinity. The results conform well with the theory of Nef that these substances result from the labile enediols that are assumed present in alkaline solutions of reducing sugars. The origin of the galacto-metasaccharinic acid from galactose is referred by Evans and Benoy to a possible rearrangement of the galactose 2,3-enediol and the suggested mechanism accounts equally well for other types of saccharinic acids that are producible from sugars. Evans and Waring have succeeded in producing the unknown hydroxypyruvic aldehyde, $CH_2OHCOCHO$, through the oxidation of dihydroxyacetone by copper acetate solution at room temperature, and its crystals (m.p. 99) were found to exist as a trimolecular polymer which depolymerized slowly in cold aqueous solution. On account of the great difficulties in preparing glyceric aldehyde, which is so important a substance in organic and especially in biochemical fields, the explicit directions and improvements of Evans and Hass, who prepared over 250 g. of the crystalline sugar by Wohl's procedure as modified by Witzemann, should prove very useful. Their careful measurements of the amounts of formic, acetic and lactic acids and pyruvic aldehyde produced from pure glyceric aldehyde in potassium hydroxide solutions are fully in harmony with the enediol theory of Nef and his students.

The enolization theory of sugar reactivity has been tested by

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[12] Paine, Birckner and Hamilton, *Ind. Eng. Chem.*, 19, 358 (1927).

[13] Goebel, *J. Biol. Chem.*, 72, 809 (1927).

[14] Evans, Edgar and Hoff, *J. Am. Chem. Soc.*, 48, 2665 (1926); Evans and Waring, *ibid.*, 2678; Evans and Hass, *ibid.*, 2703.

Gustus and Lewis[15] through the oxidation of tetramethylglucose by alkaline hydrogen peroxide solutions. Since enolization is here restricted from structural considerations to one enediol (1,2-position) the reaction would be expected to yield principally carbon dioxide, formic acid, and methylated *d*-arabonic acid. The two former were obtained in large amounts and 17% of a dimethyl-*d*-arabonic lactone was isolated, together with much smaller quantities of sugar acids of shorter carbon chains. The authors interpret their results as indicating that the principal reaction is indeed the oxidation of a 1,2-enediol, accompanied by some destruction of the sugar through the strong oxidizing conditions employed. This view leads the authors to the conclusion that the enolization of sugars takes place, not through the selective addition and loss of water as suggested by Nef, but rather through a direct keto-enol tautomerism.

Glucose and fructose are interconvertible in disodium phosphate solutions and they also yield as much as 50% of a nonfermentable sugar sirup which is apparently the same product that Lobry de Bruyn and Van Ekenstein obtained with other alkalies and designated glutose, but it is doubtful whether this material should be classed as a definite sugar and it seems more likely that it is a mixture similar to the formose obtained from the polymerization of formaldehyde in alkaline solutions.[16] A critical study of the mechanism of the oxidation of glucose to gluconic acid in alkaline solutions of iodine has been made by Goebel.[17] The epimerization of galactonic acid by water and pyridine has been accomplished by Hedenburg and Cretcher[18] through long heating at 100° (in comparison with the older autoclaving at 140° by Fischer) with the result that less decomposition occurs and a better yield of talonic acid is obtained. It proved possible in this way to obtain pure talonic acid in crystalline form, which had never before been accomplished.

Studies Relating to the Structures of the Sugars. The influence of the reactants and of acetic acid on the speed and extent of formation of glucoseanilide in alcoholic solution has been studied by Cameron,[19] and in a second article[20] it is shown that the coloration of such solutions is due to side reactions involving decomposition of the anilide and oxidation of aniline.

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[15] Gustus and Lewis, *J. Am. Chem. Soc.*, 49, 1512 (1927).
[16] Spoehr and Wilbur, *J. Biol. Chem.*, 69, 421 (1926).
[17] Goebel, *J. Biol. Chem.*, 72, 801 (1927).
[18] Hedenburg and Cretcher, *J. Am. Chem. Soc.*, 49, 478 (1927).
[19] Cameron, *J. Am. Chem. Soc.*, 48, 2233 (1926).
[20] Cameron, *J. Am. Chem. Soc.*, 48, 2737 (1926).

Monobenzoylglucuronic acid has been isolated in crystalline form for the first time from the urine of animals to which benzoic acid had been fed, and it is suggested that the benzoyl radical is attached to carbon 2 adjacent to the aldehydic end carbon.[21]

The rotation of the α-form of mannose pentaacetate led Hudson to suspect that the substance may be a mixture, but Levene and Bencowitz [22] have now purified it by nine recrystallizations and conclude that it is a pure substance.

The rotations of the pentaacetates of glucose and mannose over a wide range of concentration and in various solvents have been measured by the same authors.[23]

Lactobionic and maltobionic acids do not form 1,4-lactones in aqueous solution when liberated from their calcium salts, which agrees with Zemplen's proof, from other data, that the disaccharide union is at carbon 4 for lactose and maltose.[24] The same authors have published a preliminary article on the deamination of aminohexoses.[25]

Details of the conversion of lactose octaacetate to a chloroheptaacetate of the new disaccharide neolactose and proof that neolactose is a *d*-galactosido-*d*-altrose have been published by Kunz and Hudson.[26] In similar manner, by the action of aluminum chloride, cellobiose octaacetate has yielded a chloroheptaacetate of another new disaccharide, celtrobiose.[27]

Precise measurements of the rotations of the fluoro-, chloro-, bromo- and iodo-acetyl derivatives of cellobiose and of 4-glucosidomannose by Brauns [28] show the same regularities that he has observed for like derivatives of other sugars, and he relates the rotations with the atomic dimensions of the halogen atoms shown by X-ray measurements of alkali halide crystals. The 4-glucosidomannose has now become an accessible sugar through his striking discovery that the prolonged action of liquid anhydrous hydrofluoric acid on cellobiose octaacetate epimerizes the structure and leads to the production of fluorohexaacetyl 4-glucosidomannose in good yield.

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[21] Quick, *J. Biol. Chem.*, **69**, 549 (1926).
[22] Levene and Bencowitz, *J. Biol. Chem.*, **72**, 627 (1927).
[23] Levene and Bencowitz, *J. Biol. Chem.*, **73**, 679 (1927).
[24] Levene and Sobotka, *J. Biol. Chem.*, **71**, 471 (1927).
[25] Levene and Sobotka, *J. Biol. Chem.*, **71**, 181 (1926).
[26] Kunz and Hudson, *J. Am. Chem. Soc.*, **48**, 1978, 2435 (1926).
[27] Hudson, *J. Am. Chem. Soc.*, **48**, 2002 (1926).
[28] Brauns, *J. Am. Chem. Soc.*, **48**, 2776 (1926).

Sobotka [29] has measured the oxygen consumed in the oxidation of various methylated sugars by several of the standard reducing sugar procedures.

Levene and Meyer [30] have prepared a derivative of the aldehydic form of glucose (pentamethylglucose) by methylating glucose diethylmercaptan and subsequently removing the SH groups by hydrolysis. Levene and Meyer [31] prepared 3,5,6-trimethylglucose by the methylation of monoacetone glucose and obtained products which apparently are mixtures of at least two substances. Contrary to expectations the sugar did not reduce Fehling's solution in the cold, though it presumably is of the γ-oxide type and the authors conclude that this supposedly characteristic reaction of γ-sugars is caused by some impurity.

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[29] Sobotka, *J. Biol. Chem.*, **69**, 267 (1926).
[30] Levene and Meyer, *J. Biol. Chem.*, **69**, 175 (1926).
[31] Levene and Meyer, *J. Biol. Chem.*, **70**, 343 (1926).

Chapter XXXII.

Stereochemistry.

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In the chapter on stereochemistry will be discussed the investigations dealing with isomerisms that are explainable on the basis of differences in the spatial arrangement of parts of the molecule, problems dealing with the correlation of definite spatial arrangements with the properties of the substances, and correlation of the configurations of substances with one or more asymmetric carbon atoms with that of a simple reference substance.

The investigations which are to be reviewed may have been referred to also in the different chapters of organic chemistry. The scope of those chapters, however, is too large to permit an adequate discussion of the problems to be dealt with here. On the other hand, there is one chapter of stereochemistry which is too large and too complex to be discussed in this place, namely, the chapter on Sugars. Hence, the work on sugars is not touched upon in this section.

It may be added at the beginning that American contributions to problems of stereochemistry are comparatively small in number and a separate review of the work in this field of chemistry is desired principally in order to stimulate greater interest in problems of stereochemistry.

An article of what may be considered of most general character is that of Senior[1] of the University of Chicago, dealing with the number of stereoisomers in molecules containing several asymmetric carbon atoms. According to the existing theory, the number is 2^n as the limiting value. When internal compensation is possible, the number is reduced by the number of internally compensated forms. Senior points out the case of $(CHBrCOOH)_3$-

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[1] Senior, *Ber.*, **60B**, **73** **(1927)**.

$C - CH_3$. According to the formula 2^n, the substance should have 8 isomers, but in reality, there exist only four. According to Senior, the condition of internal compensation is absent in every one of the possible isomers. Hahn,[2] however, has pointed out that some of the possible isomers may be regarded as possessing a certain type of internal compensation, so that the general rule for determining the number of possible isomers is not contradicted by the example of Senior. Even if the view of Hahn is correct, as it seems to be, it was important to have had the question raised.

A paper dealing with one of the problems of stereochemistry which has come to notice only recently is that of Butler and Adams.[3] In the diphenyl series, isomerisms have been discovered which can be explained best by the assumption of a rigid spatial position of the two aryl groups to each other such as to permit the formation of two not superimposible isomers. The steric nature of the isomerisms in the diphenyl series was definitely proven by the brilliant work of Kenner and Stubbing[4] through which was accomplished the resolution of diphenylic acids. Butler and Adams raised the question whether the same type of isomerism occurs in the diphenylmethane series. The possibility of such isomerisms was suggested by the fact that 4,4′-diaminodiphenylmethane, similarly to benzidine, forms ring structures with carbon disulfide.

The authors therefore made an effort to resolve the following three substances: 2,2′-dicarboxydiphenylmethane, 4,4′-dinitro-2,2′-dicarboxydiphenylmethane and mononitro-2,2′-dicarboxydiphenylmethane. The result was always negative.

Jones and Wallis[5] have made a very important contribution to the question of the persistence of optical activity in free radicals. The answer to the question was affirmative on the basis of the observation on the degradation of optically active phenylmethylacetic acid to optically active phenylmethylmethylamine. The authors claim that no inversion took place in the course of the reaction. The latter conclusion, however, is in need of further corroboration.

From the viewpoint of the general behavior of stereoisomers, interesting contributions were made by Brode and Adams.[6] These authors were interested in the question as to whether fiber displays a selective adsorption towards one or the other isomer of optically active dyes. The dyes were obtained by coupling diazotized phenyl-(*p*-amino-benzoylamino)-acetic acid with β-naphthol or with dimethylaniline and by coupling diazotized *m*-aminomandelic acid with β-naphthol. The result was negative. The authors therefore concluded that their experiments failed to furnish evidence in favor of the chemical theory of dye adsorption. It may be added, however, that if in the case of Butler and Adams, the process of adsorption is analogous to salt formation, then no selective affinity of the fiber for one or another isomer can be expected.

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[2] Hahn, *Ber.*, 60, 1362 (1927).
[3] Butler and Adams, *J. Am. Chem. Soc.*, **47**, 2610 (1925).
[4] Kenner and Stubbing, *J. Chem. Soc.*, **119**, 593 (1921).
[5] Jones and Wallis, *J. Am. Chem. Soc.*, **48**, 169 (1926).
[6] Brode and Adams, *J. Am. Chem. Soc.*, **48**, 2193 (1926).

Another series of publication in the field of stereochemistry is that of Levene and his co-workers[7] dealing with correlating the configurations of substituted carboxylic acids and of secondary carbinols with the configuration of a simple reference substance, namely, of lactic acid. Thus hydroxyacids which can be readily transformed into lactic acid have been correlated with the latter by the school of E. Fischer. However, the configurations of the majority of hydroxyacids are not yet established. Levene and his co-workers undertook to correlate first the configurations of 3-hydroxybutyric acid and 4-hydroxyvaleric acid with lactic acid. The knowledge obtained in this manner permitted the correlation of the configurations of ethylmethyl carbinol with lactic acid and through the knowledge of the configuration of this carbinol, it will be possible to correlate the configuration of 2-hydroxybutyric acid with lactic acid and by an analogous process the configurations of the higher hydroxyacids.

The set of reactions by which 3-hydroxybutyric acid and methylethyl carbinol were correlated with lactic acid is shown on page 245.

The 4-hydroxyvaleric acid was correlated to lactic acid in a similar manner. For all the acids correlated to dextro-lactic acid, the direction of rotation changed towards the left on passing from the undissociated acid to the ion. The same rule was found to hold in other hydroxyacids the configuration of which has previously been correlated to that of dextro-lactic acid. The finding of Levene, Haller and Walti gives a more universal character to the above rule.

The second question raised by Levene and Mikeska was whether the above rule of shift of rotation held for carboxylic acids substi-

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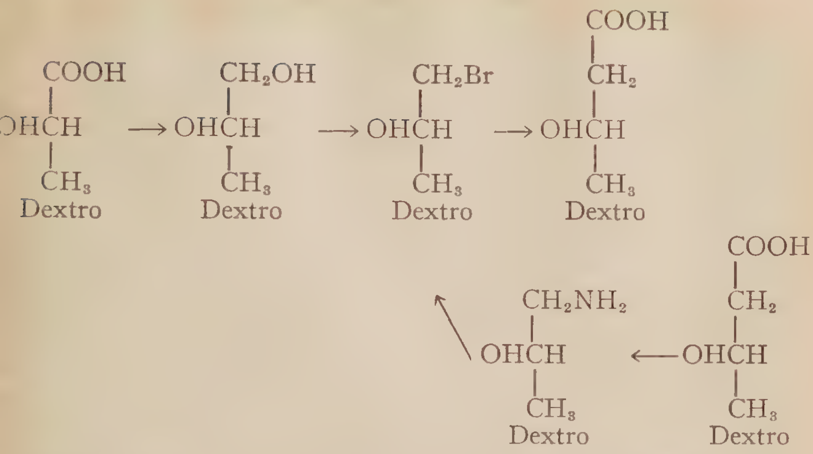
[7] Levene and Haller, *J. Biol. Chem.*, 65, 49 (1925); 67, 329 (1926); 69, 165, 569 (1926).



tuted in position (2) by groups of other polarity than OH, namely, by NH_2, Cl, SH, SO_2H, etc. That the rule holds for amino acids had been made probable by Levene [8] through his observations on 2-aminohexonic acids. Levene and Mikeska [9] have now tested the validity of the rule on a series of thiol and sulfonic acids, which were known to be configurationally related on the basis of the method of their preparation. The substances investigated by them were thiol- and sulfo-propionic acids and thiol- and sulfo-succinic acids and thiol- and sulfo-succinamide. In all these acids it was found that the change in polarity of the significant group had no effect on the character of change in the direction of rotation on passing from the undissociated acid to its ion.

In another series of investigations Levene and Mikeska [10] observed the change of rotations produced in secondary carbinols on substitution of the hydroxyl by a halogen. The changes in rotation were then compared with those produced in the corresponding thiols on their conversion into the sulfoacids.

In all pure aliphatic carbinols the substitution of the hydroxyl by a halogen was accompanied by a change of direction of rotation, also the conversion of the thiol derivatives of this group into the sulfo derivatives was accompanied by a change of direction of rotation. From this it was concluded that secondary aliphatic carbinols were configurationally related with the halides rotating in the opposite direction. Levene and Mikeska found the same rule to hold for benzylphenyl carbinol.

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[8] Levene and Walti, *J. Biol. Chem.*, 68, 415 (1926); 71, 461 (1926); Levene, Walti and Haller, *J. Biol. Chem.*, 71, 465 (1926); Levene, Haller and Walti, *J. Biol. Chem.*, 72, 591 (1927).

[9] Levene and Mikeska, *J. Biol. Chem.*, 60, 685 (1924); 63, 85 (1925); 70, 365 (1926).

[10] Levene and Mikeska, *J. Biol. Chem.*, 59, 473 (1924); 63, 85 (1925); 65, 507, 515 (1925); 70, 355, 365 (1926).

In the homologues of methylphenyl carbinol, the result of halogenation was determined by two factors, first, by the character of the aliphatic group and second, by the reagent. Thus, methylphenyl and ethylphenyl carbinols form halides of opposite sign with phosphorus pentahalide and of the same sign with thionyl chloride. On the other hand, propylphenyl, isopropylphenyl and butylphenyl carbinols form halides of the same sign with either one of the reagents. Levene and Mikeska conclude that in methylphenyl and ethylphenyl carbinols the reaction with $SOCl_2$ brings about a Walden inversion, whereas reaction with PCl_5 proceeds normally. On the other hand, in propylphenyl, isopropylphenyl and butylphenyl carbinols, halogenation is always accompanied by Walden inversion. The conclusion is based on the fact that in all the thiols of this mixed series, the conversion into the corresponding sulfonic acids is accompanied by a change of the direction of rotation.

Levene and Bass [11] report on the resolution of several *dl*-alkyl acetic acids. The *dl*-2,*n*-propyl, 2-isopropyl and 2,*n*-butylpropylacetic acids were resolved into the active components. The object was to correlate the configurations of these acids and hydrocarbons to which they may be reduced with that of the simplest member of the series of acids, namely, of methylethylacetic acid.

Levene and Walti [12] report on Walden inversion occurring on hydrolysis of optically active propylene oxide into the glycol. Previously Walden inversion had been observed only in the course of reactions of substitution. More recently Halenberg, Philips and Kenyon, Phillips and Turley and Kuhn have reported observations on Walden inversion which occur in the course of hydrolysis. Levene and Walti find that on hydrolysis of propylene oxide with alkali, the reaction proceeds without inversion whereas hydrolysis with acids brings about the inversion. The article contains a theory of the mechanism of Walden inversion.

In conclusion, two articles by Glattfeld and co-workers need be mentioned. The interest in their achievement is of a practical nature. The success of an attempt to resolve the *dl*-forms of any substance into the active components depends upon the existence of suitable reagents. Glattfeld, Hopkins and Turber[13] have prepared optically active trimethylethylaniline and Glattfeld and Cameron[14] have prepared the optically active forms of *p*-amylphenylhydrazine.

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[11] Levene and Bass, *J. Biol. Chem.*, 70, 211 (1926).
[12] Levene and Walti, *J. Biol. Chem.*, 73, 263 (1927).

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[13] Glattfeld, Hopkins and Thurber, *J. Am. Chem. Soc.*, 49, 1039 (1927).
[14] Glattfeld and Cameron, *J. Am. Chem. Soc.*, 49, 1043 (1927).

Chapter XXXIII.

Proteins.

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Since the date of the first review as well as prior to it, the most important contributions of American workers in the field of protein chemistry were devoted to physio-chemical problems, to the physiology of proteins and to the developments of analytical methods for the study of the products of hydrolysis. Comparatively little work was done on the question of the chemical structure of the protein molecule. However, this review will deal with every phase of protein chemistry separately, devoting a section to each phase, even though the number of contributions may be very small.

Synthesis of Aminoacids and of Peptides. In this connection may be mentioned first, the synthesis of new aminoacids and second, the synthesis of peptides.

On the synthesis of aminoacids a contribution was made by Osterberg[1] who synthesized α-amino-β-hydroxy- and γ-amino-β-hydroxyvaleric acids. The first was prepared by condensation of α-chloropropylethyl ether with phthalimidomalonic ester and the second by the reduction of β-hydroxylevulinic acid oxime.

Gatewood and Johnson[2] report on aminoacid derivatives containing sulfur in the amide linking ($—CS—NH—$). The new substance prepared by them is ethylthionhippurate, $C_6H_5\mathit{CSNH}CH_2COOC_2H_5$, with the ultimate object of obtaining a clearer understanding of the various forms of sulfur combinations present in the protein molecule.

In this place may also be mentioned a paper dealing with the preparation of several derivatives of *l*-cystine and of *dl*-cystine by Gortner and Hoffman.[3] The authors had previously reported an observation to the effect that *l*-cystine on prolonged boiling with 20% hydrochloric acid is racemized. The physical properties of the two substances show marked differences and the authors now find that their derivatives also show physical differences. However, in view of the fact that the attempts to resolve the inactive form thus far have been unsuccessful, the authors are inclined to attribute to the inactive form the structure of the mesocystine. One should bear in mind that simple aminoacids under similar conditions undergo racemization not unreadily and that therefore further efforts to resolve the inactive cystine should not be abandoned.

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[1] Osterberg, *J. Am. Chem. Soc.*, 49, 538 (1927).

[2] Gatewood and Johnson, *J. Am. Chem. Soc.*, 48, 2900 (1926).

[3] Gortner and Hoffman, *J. Biol. Chem.*, 72, 433 (1927).

Analytical Procedures. Considerable progress has been made in recent years in the methods of analysis of protein hydrolyzates, particularly through the efforts of Folin and his co-workers who have devised many colorimetric methods for individual aminoacids. The work is of prime importance as a prerequisite for the elucidation of the fundamental question of the structure of the protein molecule. The most recent contribution of Folin [4] in cooperation with Ciocalteu deals with the problem of the estimation of tyrosine and tryptophane in protein hydrolyzates. The work was undertaken with the object of improving the earlier methods of Folin and Looney. Folin and Ciocalteu find that the conditions of the earlier methods contained several factors which made the final result inaccurate. The new method for tyrosine estimation is based on a color test with Millon's reagent. For the details of the method, the reader is referred to the original article as the details of the procedure need to be followed very accurately. Also for the details of the tryptophane estimation the reader is referred to the original article. In this place it suffices to say that for an accurate estimate of the proportions of the aminoacids in the proteins not only the conditions of analysis have to be followed very accurately but also the conditions of hydrolysis have to be such as to give the maximum yield of the desired aminoacid,—in this case tryptophane. Folin and Ciocalteu have worked out the conditions of hydrolysis in great detail.

A second analytical method deals with the estimation of the total and labile sulfur in proteins by Maxwell, Bischoff and Blatherwick.[5] This problem has acquired special interest in connection with work on the chemical structure of insulin, to which a protein nature is attributed. The principles of the method are in part the same as those of the method of Abel. In addition, the nephelometric estimation of sulfur as barium sulfate is introduced.

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[4] Folin and Ciocalteu, *J. Biol. Chem.*, 73, 627 (1927).

[5] Maxwell, Bischoff and Blatherwick, *J. Biol. Chem.*, 72, 51 (1927).

Vickery and Leavenworth[6] and Vickery[7] have improved the methods of analysis of histidine and arginine. In the first of two articles, Vickery reports on a derivative of histidine with 2,4-dinitro-1-naphthol-7-sulfonic acid, a reagent introduced by Kossel for the isolation of arginine. The new derivative of histidine permits its isolation in pure state. In the second article with Leavenworth, Vickery describes the exact conditions for the separation of the silver salts of the two substances from each other. Previously, the method of separation was imperfect and not very accurate. The authors now find that on bringing a solution of the silver salts and an excess of silver ions to $pH = 7$, one obtains a precipitate of the silver salt of histidine and from the filtrate the silver salt of arginine settles out at $pH = 10$ to 11. The further purification of the bases can then be accomplished by 2,4-dinitro-1-naphthol-7-sulfonic acid.

The important question of the optimal conditions for hydrolysis of protein was dealt with by Greenberg and Burk.[8] The object of the writers, however, was more than practical; it aimed also to elucidate the dynamics of the hydrolysis. The conditions of hydrolysis were varied by the authors with respect to temperature and time and nature of the acid. From the table given in the publication, one may conclude that the maximum hydrolysis is obtained for hydrochloric acid at 98-100° C. with 3 *N* acid after 23 hours. With sulfuric acid of 3 *N* and 1.5 *N* concentration and $t = 98\text{-}100°$C., the maximum was not reached. At 130° C. gelatin was hydrolyzed to the maximum with 3 *N* acid in 3 hours; with 3 *N* sulfuric acid the maximum was not reached in the same interval.

As regards the dynamics of the reaction, the authors found that the hydrolysis followed the equation for a second order of reaction. It seems to the reviewer that for the mathematical treatment of the problem, the work should be repeated under conditions of greater rigor as regards the experimental conditions.

Among the publications dealing with the analytical side of protein chemistry, mention may be made also of the paper of Wilson and Lewis.[9] These authors analyzed several keratins from the viewpoint of their cystine content and found no characteristic differences. Incidentally, they compared the colorimetric method of cystine estimation of Folin and Looney with the earlier method and found an explanation for the lower values obtained by the earlier authors in the fact that it is impossible to obtain from the hydrolyzate all the cystine by the process of precipitation.

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[6] Vickery and Leavenworth, *J. Biol. Chem.*, **72**, 403 (1927).
[7] Vickery, *J. Biol. Chem.*, **71**, 303 (1927).
[8] Greenberg and Burk, *J. Am. Chem. Soc.*, **49**, 275 (1927).

Also a paper by Hetler [10] may be mentioned. This author made an estimation of the nitrogen partition according to Van Slyke on an alkali-soluble protein obtained from *Bacillus lactis aerogens* and came to the conclusion that the protein was distinct from a similar protein obtained from the *Bacillus tuberculosis*.

Work on the Structure of the Protein Molecule. Among the publications belonging to this section is the work of Brand and Sandberg [11] on dialanylcystine. It was always known that part of the sulfur contained in the protein molecule was relatively labile whereas another part was comparatively stabile. Cystine, on the other hand, does not give up its sulfur very readily. Hence, protein chemists for a long time were in search among the products of protein hydrolysis of substances with labile sulfur. (Compare the work of Gatewood and Johnson described in the section on Synthesis.) Brand and Sandberg now find that in dialanylcystine the behavior of the sulfur is very analogous to that in protein inasmuch as part of it is given off quite readily.

Levene and Pfaltz [12] published further contributions to the problem of racemization of ketopiperazines and peptides. The aim of the work was outlined in the review in the first volume of this publication. It was then pointed out that the work might find an answer to the question of the presence of ketopiperazines in the protein molecule. In the latest paper Levene and Pfaltz report on the behavior of *l*-alanylglycine anhydride and of the tetrapeptide, glycyl-levo-alanyl-levo-alanyl-glycine. In the tetrapeptide, which is composed of comparatively long chains with three peptide linkings, the racemization under the influence of dilute alkali was minimal and that only after prolonged action of the alkali. On the other hand, the racemization of the ketopiperazine proceeded as rapidly as in other ketopiperazines. The authors contemplate further work on the racemization of proteins.

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[9] Wilson and Lewis, *J. Biol. Chem.*, 73, 543 (1927).
[10] Hetler, *J. Biol. Chem.*, 72, 573 (1927).
[11] Brand and Sandberg, *J. Biol. Chem.*, 70, 381 (1926).
[12] Levene and Pfaltz, *J. Biol. Chem.*, 70, 219 (1926).

Levene, Bass, Steiger and Bencowitz[13] discuss the question of the tautomeric forms of proteins and peptides. Tautomerism in peptides is theoretically possible because of the presence of peptide linkings. The group $\underset{\substack{| \\ NH_2}}{RCH} - CO - NH - CH_2 - COOH$ theoretically permits the following 2 tautomeric forms: $\underset{\substack{| \\ NH_2}}{RCH} = COH - NHCH_2COOH$ or $RCH_2 - \underset{\substack{| \\ NH_2}}{C}(OH) = N - CH_2COOH$. Each of the tautomeric forms should then develop a new dissociation constant in addition to the two demonstrable in the usual peptides. By the aid of the optical method, Levene and Bass demonstrated a dissociation constant with a value $10^{-13.5}$ in levo-alanyl-levo-alanine anhydride. By the same method they then demonstrated the presence of a similar dissociation constant in the tetrapeptide, glycyl-levo-alanyl-levo-alanyl-glycine. From this observation the authors conclude the existence of tautomeric states in proteins in solution, under definite conditions of hydrogen ion concentration.

A result rather disconcerting to protein chemists was published by Levene, Simms and Pfaltz.[14] The future progress of our knowledge of the structure of individual proteins depends upon the discovery of methods of partial hydrolysis. The possibility of obtaining products of incomplete hydrolysis depends upon the existence of linkings of varying degrees of stability. Thus naturally a question arose as to the relationship between the structure of the amino acids and the stability of peptides formed from them. Levene, Simms and Pfaltz now find that the stabilities of peptides depend on the intrinsic dissociating constants of the amino acids. These constants have practically the same value for all amino acids containing only two ionizable groups. Thus, it seems that on partial hydrolysis of proteins, one may expect to isolate only such protein fragments as contain at least one component with more than two dissociation constants. In a way, this conclusion is supported by experience. Thus, on partial hydrolysis of proteins with acids, only the so-called kyrines were obtained. Should other enzymes display as little selective action as erepsin used by Levene, Simms and Pfaltz, the hope of obtaining on partial hydrolysis fragments composed of simple amino acids will be very slight.

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[13] Levene, Bass, Steiger and Bencowitz, *J. Biol. Chem.*, **72**, 815 (1927).
[14] Levene, Simms and Pfaltz, *J. Biol. Chem.*, **70**, 253 (1926).

Physical Chemistry of Proteins. The work on the physical chemistry of proteins was concerned principally with the determination of their molecular weights and the study of their basic and acidic functions.

Molecular weight estimations. Molecular weight estimation is an old problem and is continually being approached by better methods. The most satisfactory of the older methods was that of osmotic pressure. However, in this method, the calculations are much complicated through the phenomenon of membrane equilibrium. Svedberg approached the problem by a new method devised by him. The method depends upon the establishment of equilibrium between the centrifuging and the diffusion of the material, as the result of prolonged centrifuging at constant temperature. The conclusion of Svedberg and Nichols[15] as regards egg albumin is that moderately purified egg albumin contains an impurity of the molecular weight of 170,000 and that pure egg albumin has a molecular weight of about 34,500.

Kunitz[16] redetermined the molecular weight of gelatin by the osmotic pressure method. However, he introduced a correction for the water hydration. The latter was determined by viscosity measurements. The value for the molecular weight of gelatin obtained by Kunitz is 61,500.

Cohn and Conant[17] have reinvestigated the problem of the molecular weights of proteins in phenolic solutions. Several authors claimed that the molecular weights of proteins in solution in phenol are much lower than in water. Cohn and Conant thought the deviation could be explained by the difficulty of drying proteins. They therefore sought to determine the lowering of the freezing point of the system phenol + anhydrous calcium chloride + hydrated calcium chloride by dissolved protein. However, protein dissolved in the above solvent had no effect on its freezing point and the authors concluded that phenol is an unsuitable solvent for measuring the molecular weight of proteins.

Work on the basic and acidic functions of proteins. The work on the basic and acidic properties of proteins deserves special attention and it may be advisable in the next volume to give a special and more adequate review of the work dealing with this problem.

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[15] Svedberg and Nichols, *J. Am. Chem. Soc.*, **48**, 3081 (1926).
[16] Kunitz, *J. Gen. Physiol.*, **10**, 811 (1927).
[17] Cohn and Conant, *Proc. Nat. Acad. Sci.*, **12**, 433 (1926).

For the present the publications will be referred to only briefly. In a general way it may be stated that the new task of the chemist working in this field is to correlate the older observations (under older may be understood observations of only a few years ago) with the newer theories of solutions. A very effective effort in this direction was made by Sorensen and Linderstrom-Lang and Lund. The work of Cohn and Prentiss[18] in this country on oxyhemoglobin was stimulated to a certain extent by that of Sorensen. These authors investigated the solvent effect on oxyhemoglobin of alkali phosphates with a view of comparing the results with those of Bronsted concerning the solvent action of neutral salts on cobaltamines. The authors demonstrated the purity of their hemoglobin by the fact that its solubility was independent of the quantity of the material in the solid phase. The authors found that the solvent action of phosphates upon hemoglobin was identical with the solvent action of a neutral salt upon a bibivalent or upon a uni-quadrivalent compound. The great solubility of oxyhemoglobin in water is ascribed by them to the strong affinity constants for acid and base of certain groups in oxyhemoglobin. The small change in solubility of oxyhemoglobin effected by neutral salts suggests that but few such groups are dissociated in oxyhemoglobin in the state in which it crystallizes near the isoelectric point.

An interesting and important contribution to the same subject is the work of Austin, Sunderman and Camack[19] on the osmotic pressure of hemoglobin and of base bound by hemoglobin. The authors confirmed the earlier conclusions of Adair as regards the osmotic pressure of hemoglobin as well as regards the apparent dissociation of sodium hemoglobinate. They find that the base bound by hemoglobin is dissociated only to about half the extent of an equivalent amount BCl, or that dissociated base in the presence of hemoglobin has an activity coefficient that decreases as the salt content decreases.

In this connection mention should be made of the work of Chapman, Greenberg and Schmidt,[20] on the combination between certain dyes and proteins. The authors come to the conclusion that the substances combine stoichiometrically and that in a general way the quantity of dye absorbed is proportional to the basic components (arginine, histidine, lysine) of the protein molecule.

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[18] Cohn and Prentiss, *J. Gen. Physiol.*, 8, 619 (1925).
[19] Austin, Sunderman and Camack, *J. Biol. Chem.*, 70, 427 (1926).
[20] Chapman, Greenberg and Schmidt, *J. Biol. Chem.*, 72, 707 (1927).

They fail to find evidence of physical adsorption between pH = 2.5 and 1.0.

Stoddard[21] deals very thoroughly with the problem of solvent action of protein in affecting the solubilities of salts, lipoids, and other biologically important substances. The publication is full of interesting suggestions.

Those interested in titration of proteins will welcome the note of Northrop[22] on a convenient method for the formol titration. In order to have two titration points as sharp as possible, Northrop titrates first to pH=7, using neutral red as indicator. Formalin is then added and the solution is titrated to about pH=9.0 with phenolphthlein.

The last topic to be discussed in this section is that on colloidal behavior of proteins. Very important contributions to this topic have been made in the past and very fundamental contributions were made in the past year. Northrop and Kunitz[23] have measured the swelling pressure of gelatin. This was found to vary between 15-37°C. independent of the concentration of gelatin. They came to the conclusion that the swelling pressure is due to the osmotic pressure of a soluble constituent of gelatin held in the network of an insoluble form.

Hitchcock[24] has studied the permeability of gelatin-coated colloidal membranes. It was found that the permeability varied with the hydrogen ion concentration of the solution. It was the greatest near the isoelectric point. With increase in the concentration of alkali or acid the permeability decreases, passes through a minimum and then increases. Similar observations were made on membranes coated with other proteins. In a qualitative way the gelatin-coated membrane seemed to follow the swelling curve observed by J. Loeb.

Kunitz[16] reports on hydration of gelatin and explains that the mechanism of hydration is a purely osmotic pressure phenomenon brought about by the presence in gelatin of at least two substances, one forming the micellae, the other remaining within the micellae in the state of solution.

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[21] Stoddard, *J. Biol. Chem.*, **71**, 629 (1927).
[22] Northrop, *J. Gen. Physiol.*, **9**, 767 (1926).
[23] Northrop and Kunitz, *J. Gen. Physiol.*, **10**, 161 (1926).
[24] Hitchcock, *J. Gen. Physiol.*, **10**, 179 (1926).

Chapter XXXIV.

Biochemistry.

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Acid-Base Metabolism. The effects of various factors on the acid-base balance of the body, and of that balance on physiological functions, continue to be objects of study. Lamson and Wing[1] find that administration of alcohol and carbon tetrachloride has no effect; since ether, chloroform and nitrous oxide all cause acidosis the non-effect of alcohol and CCl_4 could not have been foretold. Hemorrhage was found by Bennett[2] to cause acidosis, with fall in both bicarbonate and pH of the blood. Koehler,[3] by oral administration of H_3PO_4, NH_4Cl, $CaCl_2$ and $(NH_4)_2HPO_4$, maintained acidosis in men for periods exceeding a fortnight, with serum pH reduced as much as 0.2 and bicarbonate to nearly half normal (an acid-base balance similar to that preceding diabetic coma, but not quite so far to the acid side as observed in actual coma). Alkalosis of corresponding degree was produced by Na citrate and bicarbonate. Subjective symptoms, nausea, headache, etc., were similar in both states. The effects on water balance were opposite, however; acidosis caused dehydration of the body and loss of weight, while alkalosis caused water retention and gain in weight. Swingle and Eisenman[4] find that adrenalectomy in cats causes acidosis, with fall in both pH and bicarbonate of the blood. Shaw[5] studied the buffer capacity of the body as a whole by measuring the amount of carbonic acid it combined with per mm. rise in CO_2 tension. He found that per gram unit the tissues are half as effective as blood, but that because of their greater bulk the total buffer effect of the tissues in the body is about 8 times that of the blood. Brocklehurst and Henderson [6] in experiments of short duration on men find, on the other hand, that the total buffer capacity of the tissues is less than that of the blood. This discrepancy in results indicates the need of further work. Gesell and Hertzman [7] devised a method for continuously recording, by means of a manganese dioxide electrode, changes in the pH of the circulating blood, and of the tissues. They found that increase in blood CO_2 tension increased acidity of both blood and tissues, but that $NaHCO_3$ injection increased the alkalinity only in the blood, the tissues (muscles) and cerebrospinal membranes being apparently impermeable to the alkali during the period of an experiment

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[1] *J. Biol. Chem.*, **69**, 349 (1926).
[2] *J. Biol. Chem.*, **69**, 675 (1926).
[3] *J. Biol. Chem.*, **72**, 99 (1927).
[4] *Am. J. Physiol.*, **79**, 679 (1927).
[5] *Am. J. Physiol.*, **79**, 91 (1926).

Analytical Methods. Griffith [8] determines hippuric acid in urine by extraction with ether, destruction of accompanying traces of urea with hypobromite, and Kjeldahl estimation of the nitrogen of the hippuric acid. Carpenter and Fox [9] have modified the Haldane gas analysis apparatus to facilitate the determination of methane together with the usual gas of expired air. Christman [10] has improved the method for allantoin. After precipitation with mercury the allantoin is treated with alkali under conditions leading to formation of 1 mol. of oxalic acid, which is estimated by titration with permanganate. Folin and Svedberg [11] have revised the Folin-Wu reagents for sugar determination, both in blood and urine. The present technique gives minimal values, indicating that the reagents are less affected by non-sugar reducing substances than the reagents formerly used. Somogyi,[12] in Shaffer's laboratory, has improved the well known Shaffer-Hartmann sugar method by using a more stable carbonate-bicarbonate buffer mixture. Behre and Benedict [13] have adapted the reaction between salicylic aldehyde and acetone to a colorimetric microdetermination of the latter. Denis and Reed [14] have improved the nephelometric Denis method for blood sulfates, and Maxwell, Bischoff, and Blatherwick [15] have applied a similar technique to micro-sulfur determination in proteins. Fink [16] has improved the electro-

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[6] *J. Biol. Chem.*, 72, 665 (1927).
[7] *Am. J. Physiol.*, 78, 206 (1926).
[8] *J. Biol. Chem.*, 69, 197 (1926).
[9] *J. Biol. Chem.*, 70, 115 (1926).
[10] *J. Biol. Chem.*, 70, 173 (1926).
[11] *J. Biol. Chem.*, 70, 405 (1926).
[12] *J. Biol. Chem.*, 70, 599 (1926).
[13] *J. Biol. Chem.*, 70, 487 (1926).
[14] *J. Biol. Chem.*, 71, 191 (1926).
[15] *J. Biol. Chem.*, 72, 51 (1927).
[16] *J. Biol. Chem.*, 72, 737 (1927).

Gutzeit micro-arsenic determination. Lee and Brown[17] have adopted magnesium perchlorate trihydrate and asbestos-sodium hydroxide to the estimation of water and CO_2 respectively in metabolism experiments. Friedmann, Cotonio, and Shaffer[18] have so improved the conditions for determining lactic acid by estimation of the aldehyde evolved from permanganate oxidation that 96 to 98 per cent of theoretical yields are obtained. Northrop[19] has refined the formol titration for estimating amino acids. Van Slyke[20] has developed an apparatus by which in 3 to 5 minutes a gas can be extracted from solution and measured, 1 per cent accuracy being attainable with as little as 0.1 cc. of gas. The apparatus is suitable for accurate micro-chemical analyses of substances in general which can be obtained in gaseous form or made to yield gaseous products. With Sendroy[21] very exact factors were worked out for use of the apparatus in determining CO_2 and carbonates. With Robscheit-Robbins[22] technique was developed for exact estimation of small amounts of carbon monoxide in blood. Kjeldahl nitrogen in amounts of 1 mg. or less is determined in the same apparatus[23] by estimating the ammonia of the Kjeldhal digest gasometrically from the N_2 evolved after treatment with hypobromite. Urea in blood or urine is determined by gasometric estimation of the CO_2 of the $(NH_4)_2CO_3$ which is formed by the action of urease.[24] Preliminary reports have been published of the determination of oxalates and of calcium by oxidizing $(COOH)_2$ to CO_2 and measuring the CO_2 gas in the apparatus (Van Slyke and Sendroy[25]), and of reducing sugars by oxidizing the latter with ferricyanide, and estimating the excess ferric iron from the nitrogen evolved by the reaction with hydrazine. $4\ Fe^{+++} + N_2H_4 \rightarrow 4\ Fe^{++} + N_2$ (Van Slyke and Hawkins[26]).

Lipoids. Levene and Rolf[27] have improved the preparation of pure lecithin through the cadmium salts. Bloor[28] studying the distribution of lipoids in muscles finds that in general the more active muscles are richer in phospholipoids, unsaponifiable lipoids,

[17] *J. Biol. Chem.*, **73**, 69 (1927).
[18] *J. Biol. Chem.*, **73**, 335 (1927).
[19] *J. Gen. Physiol.*, **9**, 767 (1926).
[20] *J. Biol. Chem.*, **73**, 121 (1927).
[21] *J. Biol. Chem.*, **73**, 127 (1927).
[22] *J. Biol. Chem.*, **72**, 39 (1927).
[23] *J. Biol. Chem.*, **71**, 235 (1927).
[24] *J. Biol. Chem.*, **73**, 695 (1927).
[25] *Proc. Soc. Exp. Biol. Med.*, **24**, 167 (1926).
[26] *Proc. Soc. Exp. Biol. Med.*, **24**, 168 (1926).
[27] *J. Biol. Chem.*, **72**, 587 (1927).
[28] *J. Biol. Chem.*, **72**, 327 (1927).

and cholesterol. Ellis and Isbell[29] find that feeding peanut and soy bean oils, respectively, caused appearance of arachidic and linolenic acids in the body fat of swine, showing some direct deposition of unchanged food fatty acids.

Organic Structure of Plant Substances. Jacobs, Hoffmann and Gustus have continued their studies of the strophanthin glucosides.[30] They show, by successive hydrolysis with an enzyme and acid, that the crystalline "K-strophanthin-β" recently isolated by them has the structure strophanthin-cymarose-glucose, the three substances being united by glucoside linkings. Additional evidence has been found concerning the nature of the double bond in the strophanthin molecule. Anderson and his colleagues[31] have identified the solid matter separating from chilled corn oil as a mixture of the myricyl esters of *n*-tetracosanic acid and an isobehenic acid.

Amino Acid Chemistry. Vickery and Leavenworth[32] have improved Kossel's separation of histidine and arginine by the silver salts. They find that the histidine salt is completely precipitated at pH 7, and the arginine salt only after enough alkali is added to raise the pH to 10 or 11.

The specific rotation of cysteine, prepared by reduction of pure *l*-cystine, is fixed by Andrews[33] at + 9.7°. Hunter and Eagles[34] claim to have improved the Folin-Looney colorimetric cystine determination, based on reduction of phosphotungstate, by using NaOH in place of Na_2CO_3 as the alkali.

Folin and Ciocalteu[35] have further studied and improved the Folin-Looney method for estimating tyrosine and tryptophane in proteins by means of Folin's molybdotungstate reagent for colorimetric phenol determinations.

Amino-Acid Physiology. Plummer, Deuel and Lusk[36] find that the effects of orally ingested glycylglycine on the rates of total metabolism and urea formation are identical with the effects of equivalent amounts of glycine. Hence it is probable that the peptide is completely hydrolyzed to glycine before absorption. Harrow and Sherwin[37] have demonstrated by rat feeding that histidine is essential for growth, but can be replaced to some extent by imidazolpyruvic acid. Lewis and Izume[38] show that when the liver is degenerated by hydrazine poisoning (rabbits) there is a loss of power to form urea, glucose, or glycogen from injected glycine. These results confirm the importance of the liver in amino acid metabolism. Rapport and Beard[39] find that valine has no accelerating effect on the metabolism of a dog, while 10 gm. of phenylalanine accelerate it 40%, and 10 gm. of tryosine 16 to 21%. Jackson[40] finds that the amounts of tryptophane sufficient to maintain rats when given by mouth do not maintain them for even 12 days when injected subcutaneously. Tryptophane in the diet could not be replaced by either *l*-β-3-indolelactic acid or 3-indole aldehyde.

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[29] *J. Biol. Chem.*, **69**, 239 (1926).
[30] *J. Biol. Chem.*, **69**, 153 (1926); **70**, 1 (1926).
[31] *J. Am. Chem. Soc.*, **49**, 1290 (1927).
[32] *J. Biol. Chem.*, **72**, 403 (1927).
[33] *J. Biol. Chem.*, **69**, 209 (1926).
[34] *J. Biol. Chem.*, **72**, 177 (1927).
[35] *J. Biol. Chem.*, **73**, 627 (1927).
[36] *J. Biol. Chem.*, **69**, 339 (1926).
[37] *J. Biol. Chem.*, **70**, 683 (1926).

Bacterial Chemistry. Heidelberger and Goebel[41] have found that the polysaccharide formed by Type III pneumococcus yields on hydrolysis chiefly a disaccharide, aldobionic acid, $C_{12}H_{20}O_{12}$, which contains one carboxyl group and one reducing group in the molecule. The polysaccharide is built up of units of this aldobionic acid.

Blood Physical Chemistry. Electrodialysis of human serum by Bernhard and Beaver[42] has shown that Na and K pass entirely to the cathode, and Cl to the anode, indicating that these substances are ionized as in simple salts. Ca, Mg, and PO_4, however, were found in both anodic and cathodic solutions, indicating that they exist partly in complex combination.

Updegraff, Greenberg, and Clark,[43] from a study of the diffusibility of serum calcium, also conclude that the "nondiffusible" portion is combined with the serum proteins in a nonionized form.

Hastings, Murray, and Sendroy[44] have exhaustively studied the conditions affecting the solubility of $CaCO_3$ and $Ca_3(PO_4)_2$ in salt solutions and serum. They find that the solubilities in salt solutions vary with the ionic strength of the latter in the manner predictable by the Debye-Hückel theory, but that the solubilities in serum are much greater. The extra solubility in serum appears partly due to the formation of slightly ionized calcium protein compounds, partly to other, as yet unidentified substance or substances, forming, like citrate, calcium compounds of low ionization.

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[38] *J. Biol. Chem.*, **71**, 33 (1926).
[39] *J. Biol. Chem.*, **73**, 299 (1927).
[40] *J. Biol. Chem.*, **73**, 523 (1927).
[41] *J. Biol. Chem.*, **70**, 613 (1926).
[42] *J. Biol. Chem.*, **69**, 113 (1926).
[43] *J. Biol. Chem.*, **71**, 87 (1926).
[44] *J. Biol. Chem.*, **71**, 723, 783, 797 (1927).

Fremont-Smith and Dailey [45] have studied the chloride distribution between human blood plasm and sterile synovial fluid, and found that in 17 out of 19 cases the distribution ratios correspond with those estimated according to Van Slyke, Wu, and McLean [46] from Donnan's theory and from the alkali binding power of the plasma proteins. The synovial fluids therefore appear to be in approximate equilibrium with the blood plasma.

Austin, Sunderman, and Camack [47] find that in solutions of sodium hemoglobinate the hemoglobin ions or molecules exert an osmotic pressure so low that the calculated molar weight is over twice that estimated on the assumption that 1 molecule of oxygen combines with 1 of hemoglobin. The pressures further indicate either that the Na combined with hemoglobin is dissociated only to about half the extent of Na in NaCl solutions, or else that, if the NaHb is completely dissociated, the activity of the Na ions is peculiarly low.

McClendon [48] has studied the electrical conductivity of whole blood and its capacity during passage of alternating currents. He concludes that the resistance and capacities of the cell membranes are such that low conductivity of the cells does not indicate impermeability to ions.

McClendon, Russell, and Tracy [49] have developed a colorimetric pH method in which ortho-chrom-T and *p*-nitrophenol are used as indicators, and advantage is taken of the Duboscq colorimeter for the readings.

Eisenman [50] introduces a gasometric plasma pH method, which is independent of indicators. Two portions of plasma are equilibrated at CO_2 tensions above and below that of the original sample, and the CO_2 contents of all 3 portions are accurately determined. By interpolation the CO_2 tension of the original is ascertained, and from the tension and CO_2 content the pH is estimated by Hasselbalch's equation, $pH = 6.12 + \log BHCO_3/H_2CO_3$.

The question of the hydration of proteins in serum has been attacked by Stoddard [51] by means of the solubilities of inert gases. The conditions are too complicated to permit a discussion of the results here.

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[45] *J. Biol. Chem.*, **70**, 779 (1926).
[46] *J. Biol. Chem.*, **56**, 765 (1923).
[47] *J. Biol. Chem.*, **70**, 427 (1926).
[48] *J. Biol. Chem.*, **69**, 733 (1926).
[49] *J. Biol. Chem.*, **70**, 705 (1926).
[50] *J. Biol. Chem.*, **71**, 611 (1927).
[51] *J. Biol. Chem.*, **71**, 629 (1927).

The studies of Henderson, Bock, and their collaborators on blood as a physico-chemical system have been continued by two papers.[52] In the first the distribution of electrolytes and water between plasma and cells of 2 normal men has been determined under the influence of varying O_2 and CO_2 tensions, and the results have been graphically expressed in nomograms showing the simultaneous changes that occur in the various factors as arterial blood changes to venous. In the second paper are shown the effects of heavy continued muscular work.

Carbohydrate Metabolism. Cori and Cori have continued their studies of intermediate carbohydrate metabolism. After feeding glucose to rats they have determined, from the gas metabolism and glycogen analyses of the tissues, the proportions of absorbed glucose burned and deposited as glycogen. They found the quotient glycogen formed/glucose oxidized to average 1.38 for normal rats, and 0.87 for insulinized ones.[53] The effect of insulin was to increase glucose oxidation at the expense of liver glycogen, the deposition of muscle glycogen being unaffected. (This effect on normal animals is quite different from that on animals with pancreatic diabetes. In the latter, insulin restores ability both to burn glucose and to store it as glycogen.) After fructose feeding normal rats deposited glycogen in their livers at the same rate as after glucose feeding.[54] Galactose feeding was followed by relatively little glycogen storage. Intravenously injected glucose was utilized by rats at a maximum hourly rate of 2.5 gm. per kilo, by rabbits at 0.9 gm. per kilo. Insulin increased the rate by 20-30 per cent. Fructose infused into the femoral vein was utilized about 1/7 as rapidly as glucose; but the rate was doubled by injection into the mesenteric vein, when the fructose went direct to the liver. After fructose feeding[55] insulin was found to decrease the ratio glycogen formed/fructose oxidized from the normal 1.16 to 0.3, the change being due to speeding up of oxidation by the excess insulin, which appears in this respect to affect the normal metabolism of fructose more than that of glucose.

Chaikoff and Macleod[56] found that when rabbits, so heavily fed with carbohydrate that their R. Q. was 1, were insulinized, there was no effect on either O_2 consumption or R. Q. Apparently insulin production in these animals had already been stimulated by food to the effective limit. Fasting rabbits, on the other hand, showed rise both in O_2 consumption and in R. Q. Barbour, Chaikoff, Macleod, and Orr [57] conclude from experiments on rats that the effect which insulin does have on the normal, carbohydrate-fed animal is to divert more of the stored carbohydrate to the muscle glycogen and less to the liver glycogen, a result agreeing with that of Cori cited above.

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[52] *J. Biol. Chem.*, **73**, 251, 749 (1927).
[53] *J. Biol. Chem.*, **70**, 557 (1926).
[54] *J. Biol. Chem.*, **70**, 577 (1926).
[55] *J. Biol. Chem.*, **73**, 555 (1927)
[56] *J. Biol. Chem.*, **73**, 725 (1927).

Reinhold and Karr [58] have studied in rabbits the relative metabolic behavior of orally administered galactose, maltose, sucrose, starch, lactose, and fructose, and found that they are effective in the order named in raising the blood sugar. This effect appears to vary directly as the rate of absorption, and inversely as the rates of oxidation and transformation to glycogen. The polysaccharides did not show the same behavior as mixtures of their component hexoses.

Lennox [59] has confirmed Foster's [60] observation that repetition of a glucose feeding within 1 or 2 hours causes in normal men a slighter increase in blood sugar than the first feeding.

Wierzuchowski [61] finds that injection of 1 gm. of phlorizin daily for 6 to 8 days is not sufficient to deprive dogs entirely of the power to utilize glucose. Appreciable increase in respiratory quotient, decrease in output of nitrogen and acetone bodies, and amelioration of symptoms (coma or convulsions) followed glucose feeding to the fasting phlorizinized animals. Olive oil feeding markedly increased the excretion of acetone bodies, as in diabetic men.

Wesson [62] finds that rats that have had their fat depots depleted by partial starvation, when fed carbohydrate will turn part of it at once into fat (respiratory quotient over 2).

Collens, Shelling, and Byron [63] find that ligation of the hepatic arteries of dogs is followed by hypoglycemic convulsions and death, with depletion of the glycogen stores of the body. The results confirm those of Mann and Magath with hepatectomized dogs, and indicate the inability of the organism in the absence of the liver to form glucose from the amino acids of broken down protein. When adrenalin was injected into the animals with ligated hepatic arteries[64] the usual rise in blood sugar did not occur, presumably from the lack of glycogen to produce it.

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[57] *Am. J. Physiol.*, **80**, 243 (1927).
[58] *J. Biol. Chem.*, **72**, 345 (1927).
[59] *J. Biol. Chem.*, **73**, 237 (1927).
[60] *J. Biol. Chem.*, **55**, 303 (1923).
[61] *J. Biol. Chem.*, **73**, 417, 445 (1927).
[62] *J. Biol. Chem.*, **73**, 507 (1927).
[63] *Am. J. Physiol.*, **78**, 349 (1926).

Izume and Lewis[65] report that hydrazine poisoning destroys the ability of the liver to store glycogen after glucose feeding: hence the abnormally high and prolonged blood sugar curves after glucose feeding. The abnormally low blood sugar content of hydrazine-poisoned fasting animals appeared due, on the other hand, to the liver's inability to synthesize glucose from amino acids.

Eagle[66] finds that normal urine contains less than 0.01 per cent of fermentable sugar. The greater amounts found by some other authors he attributes to prolonged fermentation, and consequent formation of traces of reducing material from the yeast itself.

Enzymes.—*Catalase.* Morgulis and Beber[67] have plotted the effect of temperature on the activity of beef kidney catalase. They find the optimum at about 2°, with a steady fall to 30°.

Erepsin. Levene, Simms, and Pfaltz[68] have further studied the ereptic hydrolysis of peptides, and find that the rate of hydrolysis by the enzyme depends on the relative acid and basic dissociation constants of the peptides. Asparagylglycine, which because of its high acid constant exists in neutral solutions as an anion, is not hydrolyzed, while peptides of a neutral nature are hydrolyzed at pH above 7.

Esterases. Noyes and Falk[69] have studied on 10 esters the action of extracts of the entire bodies of rats killed at varying ages. They conclude that one type of enzyme is present in the embryo, and that others are added to it during development. When the extracts stood for some time, the esterase action reverted to the embryonic type. Extracts of adult mice[70] on standing approached the esterase action of tumors, while extracts of young mice approached the embryonic type. Similar studies were made of extracts of human uterine fibroid tumors and uterine muscle.[71]

Glycogenase. Visscher[72] finds that the optimum pH for the liver glycogenase is pH 6.5, and that it is not shifted by the presence of adrenalin. This finding appears to dispose of Langfeldt's theory of the manner in which adrenalin causes hydrolysis of the liver glycogen *in vivo*.[73] Davenport[74] confirmed Visscher's results and finds that neither adrenalin nor insulin affects the activity of liver glycogenase *in vitro*.

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[64] *Am. J. Physiol.*, 79, 689 (1927).
[65] *J. Biol. Chem.*, 71, 51 (1926).
[66] *J. Biol. Chem.*, 71, 481 (1927).
[67] *J. Biol. Chem.*, 72, 91 (1927).
[68] *J. Biol. Chem.*, 70, 253 (1926).
[69] *J. Biol. Chem.*, 72, 449 (1927).
[70] *J. Biol. Chem.*, 72, 467 (1927).
[71] *J. Biol. Chem.*, 72, 475 (1927).
[72] *J. Biol. Chem.*, 69, 3 (1926).

Invertase. Nelson and Anderson[75] find that the relative effects of α- and β-glucose and fructose in retarding sucrose inversion vary with the sucrose concentration.

Pepsin. Fenger and Andrew[76] describe a satisfactory technique for preparing pepsin from hog stomachs. Goulding, Borsook, and Wasteneys[77] find that the velocity of autodestruction of pepsin is proportional to the OH ion concentration.

Urease. Sumner[78] describes the preparation of a crystalline globulin from the jack bean, which shows a tremendous activity in hydrolyzing urea to ammonium carbonate, and which he believes is identical with the enzyme urease.

Mineral Metabolism. *Calcium and Phosphorus.* Bergeim[79] finds that absorption of Ca and P in rats is but little assisted by feeding large proportions of starch, glucose, fructose or maltose, but is markedly accelerated by lactose (which is more slowly absorbed). The effect is believed to be due to lactic acid fermentation in the intestine. Lactose did not prevent development of rickets on diets high in Ca but low in P and antirachitic substance. During passage of food, acid phosphate was observed to be secreted into the upper parts of the intestine, and to be of apparent assistance in the absorption of Ca in the lower parts. Karelitz and Shohl[80] found that a diet high in Ca and low in PO_4 produced rickets in growing rats. The retention of Ca was 50 per cent normal, that of PO_4 was 30 per cent, so that an excess proportion of Ca was retained. The rickets was curable by adding PO_4 to the diet. An increased Ca retention followed, and a still greater PO_4 retention, so that the Ca : PO_4 ratios approached the normal.

Sodium and Potassium. Miller[81] finds that while the growing male rat requires 15 mg. of K per day, and the female 8 mg., the adult is maintained by 2 mg. He concludes that the K requirements for animal nutrition are satisfied by any ordinary diet. Addition of excessive amounts of K salts increased the urinary

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[73] *J. Biol. Chem.*, **46**, 381 (1921).
[74] *J. Biol. Chem.*, **70**, 625 (1926).
[75] *J. Biol. Chem.*, **69**, 443 (1926).
[76] *J. Biol. Chem.*, **73**, 371 (1927).
[77] *J. Gen. Physiol.*, **10**, 451 (1927).
[78] *J. Biol. Chem.*, **69**, 435 (1926).
[79] *J. Biol. Chem.*, **70**, 35, 51 (1926).
[80] *J. Biol. Chem.*, **73**, 655, 665 (1927).
[81] *J. Biol. Chem.*, **70**, 587, 593 (1926).

Na and Cl output. Miller[82] confirms Mitchell and Carman[83] in finding corn deficient in Na.

Nucleic Acids. Levene and Simms[84] have determined and analyzed the alkali titration curve (relation of pH to alkali added) of yeast nucleic acid, and find it indicates that there is only one secondary phosphoric acid group. This conclusion supports that formerly reached by Levene concerning the structure of yeast nucleic acid. The titration curves of animal nucleic acid prepared from thymus and spleen were also determined, and the dissociation constants of the different acid hydrogen atoms in the molecule were estimated. Levene and Bass[85] conclude from the reaction of hydrazine with the ribose-uracil nucleoside, uridine, that the ribose is attached to the nitrogen atom in position 3 of the uracil.

Chemistry of Proteins. Chapman, Greenberg, and Schmidt[86] find that acid dyes combine with dissolved gelatin in stoichiometric proportions equivalent to the free basic groups of the arginine, histidine, and lysine.

Gottenberg and Alsberg[87] find that while alcohol of strengths between 30 and 80 volume % does not alter wheat gliadin, even when warmed, alcohol below 20 or over 80 per cent changes it even in the cold.

Northrop and Kunitz[88] find that the swelling pressure of gelatin is consistent with the conception that the gelatin consists of a mixture of at least two substances, one of which is soluble in cold water, does not form a gel, and has a low viscosity and a high osmotic pressure. The second is insoluble in cold water, forms a gel in very low concentration, and swells much less than ordinary gelatin. Two fractions with the above properties were isolated from gelatin by alcoholic precipitation. Adding increasing amounts of the soluble fraction to the insoluble one results in greater swelling. Swelling of gelatin in water is apparently an osmotic phenomenon, due to the osmotic attraction of water by the soluble constituent which is held in the network of the insoluble one. Kunitz[89] furnishes further quantitative data in support of this explanation of swelling. Furthermore from the equation

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[82] *J. Biol. Chem.*, 70, 759 (1926).
[83] *J. Biol. Chem.*, 68, 165 (1926).
[84] *J. Biol. Chem.*, 70, 327 (1926).
[85] *J. Biol. Chem.*, 71, 167 (1926).
[86] *J. Biol. Chem.*, 72, 707 (1927).
[87] *J. Biol. Chem.*, 73, 581 (1927).
[88] *J. Gen. Physiol.*, 10, 161 (1926).
[89] *J. Gen. Physiol.*, 10, 811 (1927).

$\frac{\eta}{\eta_0} = \frac{1 + 0.5\,\phi}{(1 - \phi)^4}$ previously developed by Kunitz ($\eta =$ viscosity of solution, $\eta_0 =$ viscosity of solvent, $\phi =$ fraction of solution volume occupied by solute) he has been able to calculate the degree of hydration of gelatin, which increases with dilution; and to estimate the molecular weight of gelatin at 61,500.

Protein Metabolism. Murphy and Jones[90] find that the proteins of wheat bran are exceptionally rich in the essential amino acids, arginine, lysine, tryptophane, tyrosine, and cystine, and are well digested and absorbed when fed to rats. The latter grow well for the first 4 months with bran proteins as the sole protein diet, but do not reproduce successfully. Hettwer and Kriz-Hettwer[91] find that undigested serum proteins can be absorbed from the intestine of the guinea pig, particularly when the intestine is ligated, in sufficient amounts to sensitize the animal to anaphylactic shock when serum is subsequently injected.

Radiation Effects. The effects on metabolism of radiating animals or their food, previously studied by Park, Steenbock, Hess, and their collaborators, have been further investigated, and attempts have been made to ascertain the chemical effect of the radiation. Eichelberger[92] finds that radiation of human subjects with sunlight or an arc causes temporary acceleration of creatinine excretion, but not of the basal metabolic rate. Dutcher and Kruger[93] find that antirachitic properties are imparted to corn oil and to dextrin by ultraviolet radiation. Hess, Weinstock, and Sherman[94] divide irradiated cholesterol into an antirachitic fraction, soluble in liquid ammonia and not precipitated by digitonin, and an inactive fraction without these properties. Hess and Sherman[95] report that while irradiated cholesterol does not raise the normal blood calcium, nor prevent the fall in blood calcium following parathyroidectomy, it does increase Ca and P retention when added to an otherwise rickets producing diet.

Reinhard and Buchwald[96] report that treatment of cholesterol with X-rays or γ-rays changes part of the cholesterol into a substance with different absorption of ultraviolet light, and with different chemical properties: a brown wax-like material is

[90] *J. Biol. Chem.*, 69, 85 (1926).
[91] *Am. J. Physiol.*, 78, 136 (1926).
[92] *J. Biol. Chem.*, 69, 17 (1926).
[93] *J. Biol. Chem.*, 69, 277 (1926).
[94] *J. Biol. Chem.*, 70, 123 (1926).
[95] *J. Biol. Chem.*, 73, 145 (1927).
[96] *J. Biol. Chem.*, 73, 383 (1927).

formed, and the quantitative color reaction with acetic anhydride and sulfuric acid in chloroform solution diminishes.

Stedman and Mendel [97] find that purified proteins are altered by exposure to a quartz mercury lamp. They become yellow, and coagulate at a lower temperature. Supplee and Dow [98] find that the antirachitic potency of milk is increased by ultraviolet irradiation, especially the potency of winter milk, which before treatment is lower than that of summer milk. Goldblatt and Moritz [99] note that irradiation of the fat in a diet lacking the fat-soluble, growth promoting and antirachitic vitamines prolongs the life of growing rats, but does not entirely make good the deficiency. Burge and Wickwire [100] report that ultraviolet irradiation destroys insulin, and diminishes the sugar utilization of paramecia.

Sulfur Compounds. Sulfur compounds have been the subjects of active study, because of their importance in tissue oxidation, as evidenced by the glutathione of Hopkins, and by insulin, the labile sulfur of which has been demonstrated by Abel; of the necessity of cystine, or some organic sulfur compound capable of replacing it, in the diet; and of the fact that sulfuric acid has been found to be one of the metabolites retained in nephritis and partly responsible for nephritic acidosis.

Thompson and Voegtlin [101] find that over 90% of the glutathione in animal tissues is in the SH form, less than 10% in the SS form. The glutathione of the blood is limited to the cells. In the organs the content declines with age and declining metabolic activity. In tumor animals the glutathione content of tumor tissue was found equal to that of the liver (the richest organ in the body). As the tumors enlarge the glutathione content of the rest of the body declines.

Kendall and Nord [102] have studied the oxidation potentials of cystine-cysteine and reduced and oxidized glutathione systems, and have concluded that "under certain narrow but definite conditions glutathione can exist in the form of a highly reactive oxygen addition product, in which the atom of sulfur changes its state of oxidation with every addition of suitable oxidizing and reducing substances to the solution."

[97] *Am. J. Physiol.*, 77, 199 (1926).
[98] *J. Biol. Chem.*, 73, 617 (1927).
[99] *J. Biol. Chem.*, 71, 127 (1926).
[100] *J. Biol. Chem.*, 72, 827 (1927).
[101] *J. Biol. Chem.*, 70, 793, 801 (1926).
[102] *J. Biol. Chem.* 69, 295 (1926).

Lewis and Lewis [103] and Rose and Huddlestun [104] simultaneously report evidence that taurine is unable to replace cystine in the diets of rats. Although taurine is apparently formed in the body from cystine (Foster, Hooper, and Whipple [105]), the reverse reaction does not occur. Polypeptides of cystine, diglycylcystine and dialanylcystine were found able to replace cystine in the diet, although the dianhydride of dialanylcystine could not (Lewis and Lewis [106]).

Sherwin, Shiple, and Rose [107] find that cystine sulfur is 80-90% eliminated oxidized to SO_4. Introduction of a benzyl group into the SH group blocks the oxidation and causes excretion of the sulfur in its organic combination.

The cystine contents of various keratins have been determined by Wilson and Lewis [108] and found to vary from 6-8% in tortoise shell to 15-20% in hair.

Denis and Reed [109] find that experimental nephritis retards the excretion of both sulfates and organic sulfur in the urine. Loeb and Benedict [110] find by gravimetric analysis that there is 0.4 to 1.0 milli-equivalent of SO_4 per liter of normal human serum, and that in nephritis the amount multiplies parallel with that of urea.

Tissue Metabolism. Hawkins [111] has measured the rate of acid (lactic) formation by Warburg's micro-technique, in which a small piece of tissue is equilibrated with $NaHCO_3$ solution and the acid formed is estimated by the increase in CO_2 tension. He found that "normal tissues produce very little acid, embryonic tissues and placenta slightly more, and malignant tumor tissues still more." The rate of anaerobic formation of lactic acid from glycogen appears to parallel the rate of growth of the tissue.

Fenn [112] has measured the oxygen consumption of frogs' nerves, and shown that it is increased 26% by electrical stimulation of the nerves.

[103] *J. Biol. Chem.*, **69**, 589 (1926).
[104] *J. Biol. Chem.*, **69**, 599 (1926).
[105] *J. Biol. Chem.*, **38**, 421 (1919).
[106] *J. Biol. Chem.*, **73**, 535 (1927).
[107] *J. Biol. Chem.*, **73**, 607 (1927).
[108] *J. Biol. Chem.*, **73**, 543 (1927).
[109] *J. Biol. Chem.*, **73**, 41 (1927).
[110] *J. Clin. Investigation*, **4**, 33 (1927).
[111] *J. Gen. Physiol.*, **9**, 771 (1926).
[112] *J. Gen. Physiol.*, **10**, 767 (1927).

Chapter XXXV.

Fixation of Atmospheric Nitrogen.

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The first attempt to apply the combined results of experiment and theory to the fixation of atmospheric nitrogen on an industrial scale, was made in 1902 at Niagara Falls, N. Y. The progress that has been made during the following twenty-five year period is shown in two papers by Ernst,[1] one historical and the other statistical, while the effect of such progress is discussed by Curtis.[2]

Although a number of processes have been reported and tried, only three, *viz.*, the arc, the cyanamide, and the direct synthetic ammonia processes, have become factors in the world's inorganic nitrogen supply. A general review of these three processes with rather particular emphasis on the Government's activities at Muscle Shoals is given by Cottrell,[3] while Braham [4] has described these processes technically.

The Arc Process. The fundamental reaction of the arc process is expressed by the equation: $N_2 + O_2 \rightleftarrows 2NO - 43{,}200$ cal. The yield of nitrogen oxides from this operation is relatively small. Although the chemical energy absorbed per metric ton of nitrogen is but 1800 kw. hrs., the total energy consumption is some 64,000 kw. hrs. This arc furnace gas, after being cooled, is passed through a series of towers in which the principal reactions are represented by the following equations: $2NO + O_2 \rightleftarrows 2NO_2 + 27{,}800$ cal. $2NO_2 + H_2O \rightleftarrows HNO_2 + HNO_3$, $3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O$, or $3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO$.

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[1] *Trans. Am. Electrochem. Soc.*, 51, Preprint (1927); *Ind. Eng. Chem.*, 19, 196 (1927).

[2] National Fertilizer Assoc., Bulletins, 1926.

[3] *Tech. Eng. News*, 5, 54 (May, 1924).

[4] Bur. Foreign Domestic Commerce, Trade Information Bull., No. 240 (1924).

The operation of the small arc plant at Le Grande, Washington, for the manufacture of sodium nitrite is described by Benson.[5]

Although the fixation of nitrogen by the arc process is not usually considered as being commercially practicable for this country, a relatively large amount of investigational work on the arc and related phenomena has been undertaken. The information thus gained can be used in explaining the mechanism of reactions which occur in the other methods of nitrogen fixation, where the phenomena cannot be so readily separated and investigated. As examples of such phenomena there are (1) activation of surfaces and gases, (2) dissociation of molecules into atoms, (3) energy transfer accompanying chemical action, and (4) collision mechanism, including excitation, ionization and radiation. The results of some of these investigations are reported by McEachron and George,[6] Tartar and Perkins,[7] and Karrer.[8]

Cyanamide Process. The commercial adaptation of the cyanamide process in 1905 followed closely such adaptation of the arc process, and the former process quickly surpassed the latter in installed capacity. The principal operations in the production of cyanamide are represented by the equations: $CaO + 3C = CaC_2 + CO - 121{,}000$ cal., $CaC_2 + N_2 = CaCN_2 + C + 98{,}430$ cal. For the first reaction Yee[9] has worked out a method for the determination of calcium carbide. The mechanism and thermochemistry of the second reaction have been studied by Krase,[10] while Jacob[11] has reported on the decomposition of the product of this reaction, calcium cyanamide, in storage. Methods for the determination of cyanamide and the preparation of cyanamide hydrochloride are discussed in two papers by Pinck,[12] while Garby[13] has reported methods for the determination of dicyanodiamide and of biguanide. Investigational work on calcium cyanamide derivatives and conversion products has been frequently reported, but this it seems is getting away from the field of nitrogen fixation and will not be discussed here. The process itself, particularly during these later years, has not been the subject of investigation. The principal progress made as shown by Landis,[14] is in economies of operation resulting in an increased yield of nitrogen fixed per unit of electrical energy employed.

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[5] *Trans. Am. Electrochem. Soc.*, **48**, 233 (1925).
[6] Bull. Purdue Univ., **6**, 1 (1922).
[7] *J. Phys. Chem.*, **30**, 595 (1926).
[8] *Trans. Am. Electrochem. Soc.*, **48**, 223 (1925).
[9] *J. Am. Chem. Soc.*, **46**, 1389 (1924).
[10] *J. Am. Chem. Soc.*, **46**, 1358 (1924).
[11] *Ind. Eng. Chem.*, **16**, 684 (1924).
[12] *Ind. Eng. Chem.*, **17**, 459 (1925); **18**, 629 (1926).
[13] *Ind. Eng. Chem.*, **17**, 266 (1925); **18**, 819 (1926).
[14] *Trans. Am. Electrochem. Soc.*, **51**, Preprint (1927).

Direct Synthetic Ammonia Process. The first industrial plant for the fixation of nitrogen according to the direct synthetic ammonia process was started into operation at Oppau, Germany, in 1913. Today the installed capacity of this process is more than double that of the arc and cyanamide processes combined. The reaction is represented by the equation: $N_2 + 3H_2 = 2NH_3 + 23,780$ cal. A general discussion of the process is given by Larson [15] and also by Powell,[16] while Pope [17] describes diagrammatically the various methods of operation, *viz.*, Haber, Claude, Casale, etc. Although the first industrial plant of this process in the United States was erected in 1921, an earlier plant, U. S. Nitrate Plant No. 1, was erected in 1917-18 for the war emergency. A detailed description of this plant, together with a comparison of it with the German plant, is given by Tour.[18]

Since the synthesis of ammonia from its elements is accomplished at elevated temperatures and pressures ranging in industry from 100 atmospheres to 900 atmospheres, many engineering and metallurgical problems had to be overcome. A detailed engineering and equipment design discussion of an operating commercial synthetic ammonia plant, was presented by Ernst, Reed and Edwards,[19] while some equipment and materials suggestions for high pressure gas work are given in several papers by Thompson,[20] Vanick,[21] and Ernst,[22] who has also presented a paper on investment and production costs.[23] The catalyst necessary for this reaction has often been called the heart of the process, and has been the subject of a large amount of investigational work. Larson [24] discusses in several papers various catalytic materials and the manufacture of a catalyst, while Wyckoff [25] has reported on some X-ray examinations of catalysts. The rate of reduction of metallic oxides has been investigated by Emmett.[26]

A study of catalysts to determine the effect of promoters has been reported by Almquist,[27] who has also discussed the poisoning action of oxygen. The equipment and the assembling of the equipment necessary for catalyst testing are of great importance as is shown by Killeffer [28] in his description of the catalyst testing plant of Lazote, Inc. The ammonia equilibrium has been investigated by Larson [29] for a pressure range of 10 atmospheres to 1000 atmospheres.

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[15] *Army Ordnance*, **4**, 21 (1923).
[16] *Refrigerating Eng.*, **12**, 180 (1925).
[17] *Refrigerating Eng.*, **12**, 209 (1926).
[18] *Chem. Met. Eng.*, **26**, 245, 307, 359, 411, 463 (1922).
[19] *Ind. Eng. Chem.*, **17**, 775 (1925).
[20] *Trans. Am. Electrochem. Soc.*, **50**, Preprint (1926).
[21] *Proc. Am. Soc. Testing Materials*, **24**, II, 348 (1924).
[22] *Ind. Eng. Chem.*, **18**, 664 (1926); Compressed Gas Manuf. Assoc., Annual Rept., 1926; *Mech. Eng.*, **48**, 595 (1926).
[23] *Trans. Am. Inst. Chem. Eng.*, **17**, 1 (1925).
[24] *Ind. Eng. Chem.*, **16**, 1002 (1924); **17**, 971 (1925); **18**, 1305 (1926).
[25] *J. Am. Chem. Soc.*, **47**, 2866 (1925).
[26] *Trans. Am. Electrochem. Soc.*, **51**, Preprint (1927).

Although the direct synthetic ammonia process is a nitrogen fixation process, hydrogen, the gas with which the nitrogen is fixed, is the more important economically. Hydrogen from water gas is discussed by Evans,[30] while Dodge [31] has reported on the feasibility of coke oven hydrogen. Jones,[32] in a paper before the International Coal Congress, pointed out that in nitrogen fixation today, coal and coke rather than hydroelectric power are the important factors. Coal, coke or power may be used for hydrogen production.

The problem of the purification of the gas mixture before being brought into contact with the catalyst is a most important one. The removal of oxygen and ultra-purification are discussed in two papers by Almquist [33] while Krase [34] has studied the removal of carbon dioxide. Benton [35] has also reported on the catalytic synthesis of water vapor, a step in the purification of the gases.

The scientific investigator and designing engineer alike are pleased to see the work of Bartlett [36] on properties of gases and gas mixtures at elevated pressures appearing in published form. There has been very little work reported on this and in fact there are but very few laboratories fitted up for such work. A publication "Relations Between the Temperatures, Pressures and Densities of Gases" contains a valuable bibliography of some 700 references on properties of gases.[37]

Investigations on the thermionic properties of ammonia catalysts by Kunsman [38] with the view of obtaining further information on the nature of the synthesis of ammonia, have shown that iron base promoted catalysts furnish very good sources of positive ions of the alkali and alkaline earth metals.

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[27] *Ind. Eng. Chem.*, **18**, 1307 (1926); *J. Am. Chem. Soc.*, **48**, 2814, 2820 (1926).
[28] *Ind. Eng. Chem.*, **17**, 820 (1925).
[29] *J. Am. Chem. Soc.*, **45**, 2918 (1923); **46**, 367 (1924).
[30] *Ind. Eng. Chem.*, **18**, 513 (1926).
[31] *Chem. Met. Eng.*, **33**, 416 (1926).
[32] Proceedings International Conference on Bituminous Coal, p. 505 (1926).
[33] *Ind. Eng. Chem.*, **18**, 866 (1926); *Chem. Met. Eng.*, **33**, 89 (1926).
[34] *Ind. Eng. Chem.*, **19**, 208 (1927).
[35] *J. Am. Chem. Soc.*, **48**, 632 (1926).
[36] *J. Am. Chem. Soc.*, **49**, 65, 687 (1927).
[37] Bur. Standards, Circular No. 279 (1926).
[38] *Phys. Rev.*, **25**, 892 (1925); **27**, 249, 737 (1926); *Science*, **62**, 269 (1925); *J. Phys. Chem.*, **30**, 525 (1926); *Proc. Nat. Acad. Sci.*, **12**, 659 (1926); *J. Franklin Inst.*, **203**, 635 (1927).

Other Fixation Processes. An investigation on the fixation of nitrogen as aluminum nitride by Krase[39] has indicated that, economically at least, the aluminum nitride process is primarily one for the production of alumina and not a nitrogen fixation process. In like manner the work of Guernsey[40] has indicated that the sodium cyanide process is not primarily a nitrogen fixation process.

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[39] *Ind. Eng. Chem.*, **18**, 1287 (1926).

[40] *J. Am. Chem. Soc.*, **47**, 1932 (1925); *Ind. Eng. Chem.*, **18**, 243 (1926).

Chapter XXXVI.

Water and Sewage.

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Continuing the work on methods of water analysis, a committee of the American Water Works Association (Hinman, chairman)[1] reports good results from brilliant green and eosin methylene blue, in the differentiation of the coli group. Ruchhoft[2] states that with the use of brilliant green bile medium on Lake Michigan water at Chicago, two days are saved in the complete confirmation of *B. coli* and that the brilliant green medium has been adopted for routine work at Chicago. Improvements in methods of water analysis[1] are suggested which have not been been adopted and which may modify methods of determining turbidity, dissolved oxygen, chlorine, carbon dioxide, and biochemical oxygen demand. Berry[3] furnishes considerable data to show that lactose fermenting bacteria which do not produce gas in 24 hours are without significance.

The question of maintaining the quality of the water at Chicago has become so acute that Ericson[4] has recommended that filtration be considered.

Preliminary experiments on the treatment of Lake Michigan water for Chicago are being made by Baylis.[5] Aluminum sulfate or iron sulfate and lime can be used for clarification. The hardness can be reduced to 50 p.p.m. by lime. From the result of studies at an experimental water purification plant of the U. S. Public Health Service, Moss and Streator[6] suggest that the *B. coli* index in raw water to be filtered be fixed at 100 in 100 cc. For water to be chlorinated the index may be 6000 in 100 cc. Further experimental work is necessary.

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[1] *J. Am. Water Works Assoc.*, **17**, 112-26 (1927).
[2] *J. Am. Water Works Assoc.*, **16**, 778 (1926).
[3] *Am. J. Pub. Health*, **16**, 590 (1926).
[4] *Eng. Cont.*, **65**, 173 (1926).
[5] *J. Am. Water Works Assoc.*, **17**, 710 (1927).
[6] Pub. Health Reports, **41**, 2121, 2129 (1926).

Levine and Soppeland [7] have found 36 varieties of bacteria in creamery wastes, 58.5% being proteolytic. Ellis [8] suggests that sulfur bacteria may be used as indicators of polluted waters. Beggiatoa, forming a grayish white felty covering on the bottom of streams, is an indication of sewage pollution. Montfort [9] has removed iron and manganese and chlorinated a water to prevent the growth of crenothrix.

There is an apparent exchange of practice in water filtration east and west. Macqueen [10] describes mechanical filters at Washington, D. C., which supplement slow sand filters. Harris [11] describes the settling basins and sand filters, to be washed with a Blaisdell sand washing apparatus, to purify the turbid Colorado River water at a rate of 22.7 million gallons per acre per day.

An improved method for the determination of hydrogen sulfide in water is described by Badger.[12] Statements by Hale and Muer [13] indicate that copper used in watershed treatment is found in the distribution system.

Chlorination has been studied widely during the year. Thorough studies have been undertaken at Schenectady by Cohn.[14] Double and triple chlorination has been used in New York by Brush.[15] Harrison [16] claims that superchlorination to avoid chlorophenol tastes is not satisfactory and a substitute for chlorine should be found. McAmis [17] did not find double chlorination satisfactory for removing the taste and recommends the addition of 0.1 to 0.2 parts per million of ammonia. Howard and Thompson [18] have made tastes unobjectionable at Toronto by superchlorination and dechlorination with sulfur dioxide. According to Cohen [19] chlorine can be used as an algacide, but is expensive.

Heath [20] emphasizes what is becoming a general practice: circulation, filtration, and chlorination for the treatment of swimming pools. 0.2 parts per million residual chlorine is sufficient.

[7] Iowa State College, Bull., 77.
[8] *Engineering*, 122, 231 (1926).
[9] *Eng. Cont.*, 65, 169 (1926).
[10] *Pub. Works*, 57, 197 (1926).
[11] *Eng. News-Rec.*, 96, 896 (1926).
[12] *J. Assoc. Official Agr. Chem.*, 9, 125 (1926).
[13] *J. Am. Water Works Assoc.*, 15, 650 (1926).
[14] *Eng. News-Rec.*, 96, 943, 1035; 97, 436 (1926).
[15] *Eng. Cont.*, 66, 47 (1927).
[16] *J. Am. Water Works Assoc.*, 17, 336 (1927).
[17] *J. Am. Water Works Assoc.*, 17, 341 (1927).
[18] *Water and Water Eng.*, 29, 61 (1927).
[19] *J. Am. Water Works Assoc.*, 17, 444 (1927).
[20] *Can. Eng.*, 20, 50, 499 (1926).

Thurma[21] removes taste and odors by aeration using 6000 cu. ft. per million gallons of water. Jenks[22] using a home-made electrolytic chlorination apparatus at Sacramento claims economy over liquid chlorine. Chandler[23] improves coagulation by adding to a colored water a water with a higher alkalinity containing algae of siliceous character and color in larger particles.

The relation of iodine and goiter is still a topic for discussion. Daniels[24] has examined the iodine content in water supplies and compared it with the distribution of goiter in Pennsylvania. He states that it is not possible to establish a relation between iodine and goiter. McClendon[25] states that one part of iodine in 100 million parts of water prevents goiter. Johnson[26] reports that iodine is given to the school children of Anaconda through the water supply and by tablets.

Chemical and biological investigations of streams and lakes have been continued. Birge and Juday[27] find about fifteen parts per million of organic matter in Wisconsin lakes. Only a comparatively small part of this organic matter is in the living plankton.

If possible, it is better to dispose of the waste matter of industrial processes at a profit within the plant than to allow it to escape to the sewer or stream. Very expensive purification plants must sometimes be built to protect water supplies. McNamee[28] shows that evaporation of 10% of a waste from a Myers still, 0.1% of the total waste, eliminated 92% of the taste producing constituents.

Boiler feed water studies are being made by a joint research committee, Powell, general chairman, representing the American Railway Engineering Association, the American Water Works Association, the National Electric Light Association, the American Society for Testing Materials, and the American Society of Mechanical Engineers.[29] Reports have been made by various subcommittees. Knowles shows that the regular operation of intermittent and continuous lime soda softeners does not differ. Lime soda preliminary to zeolites is good in large plants for the pretreatment of boiler feed waters. Foulk tells of the present knowledge of foaming and priming.[29, 30] Progress reports of other committees have been made. Several papers were presented before the meeting of the American Water Works Association in June, 1927, but the papers have not yet been published.

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[21] *Water Works,* **66**, 124 (1927).
[22] *Eng. News-Rec.,* **97**, 170, 843 (1926).
[23] *J. Am. Water Works Assoc.,* **16**, 181 (1926).
[24] *J. Am. Water Works Assoc.,* **16**, 227 (1926).
[25] *J. Am. Water Works Assoc.,* **15**, 222 (1926).
[26] *J. Am. Water Works Assoc.,* **16**, 205, 1926.
[27] *Proc. Nat. Acad. Sci.,* **12**, 515 (1926).
[28] *Eng. News-Rec.,* **97**, 95 (1926).
[29] *Mechanical Engineering,* **48**, 136 (1926).

Sturdevant [31] states that nine zeolite water softening plants are in operation on the Southern Pacific Railroad. While there is some foaming, there has been no embrittlement, no corrosion, and a reduced cost in boiler maintenance. Waters high in calcium and magnesium should be treated first with lime.

The use of zeolites in water softening for municipal supplies is beginning. Beech [32] describes the water softening plant used by the Ohio Valley Water Co. Other installations are being considered.

Hoover,[33] after making experiments with a combination of lime treatment preceding zeolite, will equip one of the Columbus filters with zeolite and make further experimental study of its value for municipal water softening. It is expected that part of the water will be reduced to zero hardness and mixed with equal part of water with 160 parts per million to produce a final effluent having 80 parts per million of hardness.

Greer and Parker [34] claim that potentiometric determinations of hydrogen ion concentration as applied to boiler waters have more value than alkalinity determinations.

Corrosion has received considerable attention. Coughlan [35] recommends excess of lime and soda to prevent corrosion in railroad water treatment. Risley [36] recommends vacuum heating to remove dissolved oxygen from water. Pownall [37] gives a summary of the causes and proposes remedies for pitting of locomotive boilers, a very important item to the railroads. Gunderson [38] calls corrosion an electrochemical phenomenon. To inhibit corrosion the H-ion concentration should be reduced to a minimum, oxygen removed from the water or anti-corrosive influences established adjacent to interior boiler surfaces by electrical means. Experiments show that a coating of arsenic affords protection.

The softening of water supplies used by municipalities is be-

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[30] *J. Am. Water Works Assoc.*, **17**, 160 (1927).

[31] *Railway Age*, **81**, 15, 675 (1926).

[32] *J. Am. Water Works Assoc.*, **15**, 227 (1926).

[33] *Water Works*, 66, 223 (1927); *J. Am. Water Works Assoc.*, **17**, 751 (1927).

[34] *Mech. Eng.*, **48**, 1129 (1926).

[35] *J. Western Soc. Eng.*, **31**, 392 (1926).

[36] *Chem. Met. Eng.*, **33**, 163 (1926).

[37] *Ry. Rev.*, **79**, 263 (1926).

[38] *Ry. Rev.*, **79**, 335 (1926).

coming more and more common. Danielson[39] reports that the hardness of the water supply of Hinsdale, Ill., is reduced from 472 to 100 parts per million in the new water softening plant at a cost of 6c per thousand gallons. Hoover[40] states that the water supply of Columbus, Ohio, is softened from 298 to 92 parts per million at a total cost for chemicals of $20.98 per million gallons. Flentje[41] reports that excess lime treatment precipitated magnesium and saved two thirds of the iron sulfate and filter alum, effecting a saving in the cost of treatment and producing a softer water. The water is recarbonated with flue gases.

The use of sodium aluminate which has been on the market for water treatment for only a few years is being continued. Barnett and Haux[42] find it has a higher coagulation efficiency, gives slight reduction in hardness, permits elimination of lime and soda, and shows no after reactions. In a discussion of the general aspects of water treatment for railroads, Bardwell[43] states that sodium aluminate breaks up soluble double salts of magnesium reducing the scaly material to 1-1½ grains per gallon.

Whipple[44] reports that the return of sludge to coagulation basin at Cambridge was not successful.

Sewage treatment in dry regions where the effluent can be used for irrigation seems ideal. Roberts and Jones[45] report irrigation with treated sewage in western Texas. The effluent from Imhoff tanks and sprinkling filters is used on a farm. The cost including interest and pumping amounts to $21.37 per acre per year. The land is rented for farming purposes.

Different methods of sludge disposal are advocated. Clifford[46] disposes of 50,000 gallons of 90% water sludge to an acre, distributing it in gutters made with a ridge plough 8 to 10 feet apart. Browne and Jones[47] used glass covered beds which have three times the capacity of open beds and less than three times the cost and can be operated independently of the weather. It would seem that the difference in capacity should be greater in order to warrant general use.

Different methods of waste disposal are suitable for different

[39] *Eng. News-Rec.*, **97**, 780 (1926).
[40] *Eng. Cont.*, **65**, 498 (1926).
[41] *J. Am. Water Works Assoc.*, **17**, 253 (1927).
[42] *Can. Eng.*, **51**, 725 (1926).
[43] *J. Western Soc. Eng.*, **31**, 392 (1926).
[44] *Water Works*, **66**, 121 (1927).
[45] *Eng. News-Rec.*, **97**, 1026 (1926).
[46] *Can. Eng.*, **51**, 299 (1926).
[47] *Pub. Works*, **57**, 308-11 (1926).

wastes. Mohlman[48] recommends activated sludge for packing house waste, settling and dilution for tannery wastes, and sprinkling filters for starch factory wastes. Bartow[49] recommends disposal as far as possible by utilization within the plant the wastes from various organic manufactures. Hadley[50] disposes of wastes from mercerizing, bleaching, and dyeing of cotton goods by treatment with lime and sulfate of aluminum. Snell and Bruce[51] state that dye wastes, when they must be treated, can be handled by various combinations of coagulation, bleaching, neutralization, evaporation, and sludge settling. Shaetzle and Powell[52] give methods for the disposal of molasses slop, rolling mill wastes, creamery, and tannery wastes.

A considerable number of sewage disposal plants by the activated sludge process are now in operation. Veatch[53] tells of the disposal of excess of sludge in California plants by returning it to the Imhoff tanks for digestion. Roberts[54] favors drying on sand beds, and recommends this process for the dry regions of the Pacific coast where the effluent can be used for irrigation. Separate sludge digestion is recommended for small towns by Donahue.[55] Cohn[56] tells of the marketing of sewage sludge after drying at Schenectady. It is sold at a nominal price of 25c per load.

Rudolfs[57] recommends the keeping of not to exceed 2 parts of fresh dry sludge to 98 parts of ripe sludge in the digestion chamber. With more than two parts, results are not satisfactory. The hydrogen ion concentration should be kept at 7.3.

Buswell and Strickhouser,[58] after examining some gases from Imhoff tanks, state that the amount and heating value warrant its collection for fuel. Hatfield[59] describes the installation at Decatur, Ill., where all the gas from Imhoff tanks is collected and burned to remove odors. The waste is very strong because of starch factory wastes. 100,000 to 125,000 cu. ft. of gas are collected daily from approximately 10,000,000 gallons of sewage. The gas contains 70 to 80% methane and from 20 to 30% carbon dioxide and nitrogen. The calculated calorific value of the gas is about 700 B t u per cu. ft. and it can be used to generate power.

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[48] *J. Western Soc. Eng.*, **31**, 267 (1926); *Ind. Eng. Chem.*, **18**, 1076 (1926).

[49] *Ind. Eng. Chem.*, **18**, 1085 (1926).

[50] *Ind. Eng. Chem.*, **19**, 239 (1927).

[51] *Am. Dyestuffs Rept.*, **16**, 54, 86 (1927); *Ind. Eng. Chem.*, **19**, 237 (1927).

[52] *Eng. Cont.*, **65**, 319 (1926).

[53] *Eng. News-Rec.*, **97**, 10 (1926).

[54] *Pub. Works*, **57**, 378 (1926).

[55] *Eng. News-Rec.*, **96**, 690 (1926).

[56] *Eng. News-Rec.*, **97**, 252 (1926).

[57] *Am. J. Pub. Health*, **16**, 500 (1926).

[58] *Ind. Eng. Chem.*, **18**, 407 (1926).

[59] *Eng. News-Rec.*, **96**, 645 (1926); *Water Works*, **66**, 99 (1927).

Garbage disposal is receiving attention. The papers presented before the Sanitary Engineering Division of the American Society of Civil Engineers[60] by Greeley, Rich, Knowlton, Boniface, Burnett, and Lewis give very complete statements of the present systems.

Burden[61] tells of a very comprehensive plan outlined for smoke abatement in St. Louis.

RESEARCH PROBLEMS

Work reported during the year shows both new and old problems which may be profitably studied. The following suggestions are made:

1. Continuation of study of methods for the identification of the colon group.
2. The significance of the colon index for polluted waters that must be used for water supplies.
3. Chlorination, double chlorination, super chlorination, and de-chlorination need further attention.
4. The relation of iodine content of water to goiter is still a subject of controversy.
5. The conditions of streams receiving sewage and trade waste need further attention.
6. Methods for the disposal of trade wastes before and after leaving the plant.
7. Boiler waters including the cause and prevention of scaling, foaming, priming, corrosion, and embrittlement.
8. The softening of water and its advantages to manufacturers, railroads, and municipalities.
9. The zeolite or base exchange method of softening water including its relation to other methods of softening.
10. The dewatering and drying of sludge both from Imhoff tanks and from the activated sludge process need further attention.
11. The use of gases from Imhoff tanks as a source of heat and power.
12. Can activated sludge be successfully digested in Imhoff tanks and the amount of gas increased for use for heat and power?

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[60] *Proc. Am. Soc. Civil Eng.*, **52**, 1642-78 (1926).
[61] *J. Am. Soc. Heating Ventilating Eng.*, **33**, 105 (1927).

Chapter XXXVII.

Fermentation Industries.

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The past year has brought forth no new or startling developments in the fermentation field. Progress has been rather of a healthy, steady character. Several new plants of importance have started production and so far as figures for the period are available at the present time, there has been increased production in the most important branches. During July, 1926, the Eastern Alcohol Corporation's new plant at Deepwater Point, New Jersey, having a daily capacity of 36,000 gallons of ethyl alcohol, was put into operation. It might be mentioned that this is the first new ethyl alcohol plant to be erected since the World War and embodies the latest improvements that have been developed in the manufacture of ethyl alcohol from molasses fermentation. Due to the greatly increased demand for nitrocellulose lacquer solvents, the Commercial Solvents Corporation put into operation, during March, 1927, at Peoria, Illinois, a new plant for the production of butyl alcohol and acetone.

Up to the present time synthetic ethyl alcohol and synthetic butyl alcohol have not made serious inroads upon fermentation products in this country, due largely to the low cost of carbohydrate materials. Conditions must change greatly before fermentation alcohols will feel the competition of synthetic alcohols domestically produced. However, in other countries where carbohydrate materials are in greater demand for food purposes the question of competition between these two processes has become more serious. Hale[1] calls attention to recent imports of synthetic butyl acetate and states that the importation of one single gallon of butyl alcohol or its derivative, butyl acetate, means that exactly one bushel of the American farmer's corn has been driven from the American chemical industry. Jones[2] reports that the Campagnie des Mines de Bethune in France is in a position to produce 5 metric tons per day of 97-98% synthetic ethyl alcohol and that preparations are being made to double the present rate of production.

Little attention is as yet being devoted in this country to the production of alcohol for the purpose of developing power. Considerable work is being carried out on this subject in other countries[3] and it seems probable that eventually the fermentation industries in America will turn their attention to this use which would result in a wide expansion of the industry.

Dean[4] gives a rather brief but good description of the modern process of making ethyl alcohol from molasses, the raw material now being largely used. He deals also with the sources and methods of transporting raw materials and other factors of interest. Killifer[5] gives a very interesting description of the plants and process of manufacturing butyl alcohol and acetone by fermentation, using corn as the raw material. Chatfield[6] points out the varied uses of industrial alcohol and the necessity of this product to the industry. Arnstein[7] gives a very complete survey of the uses of industrial alcohol. Orr[8] deals with the production and uses of butyl alcohol in a recent article.

Technical developments relating to the ethyl alcohol industry recorded in the literature have not been very extensive during the course of the past year. Reich[9] describes a process for the recovery of alcohol, organic acids and fertilizer from fermented saccharine materials. His process consists of neutralizing the fermentation liquid, distilling the latter to obtain the alcohol, and finally calcining the residue to recover the organic acids. Owen and Bennett[10] found that bagasse which was first extracted with water and then treated with a sugar solution comparable in composition to a cane juice did not depress the yield of alcohol from a molasses wort, and that the overall efficiency of the mixture of bagasse and molasses solution was practically as good as on the molasses alone. This indicates that with fresh bagasse satisfactory yields of alcohol could be obtained. Zeller[11] in a study of the effect of buffers on alcoholic fermentation found that the presence of ammonium salts such as phosphate, oxalate, carbonate, citrate, tartrate and formate in the fermentation liquid increases the activity of pressed yeast by 80 to 140%. The chloride, bromide, iodide, benzoate, etc., function in the same way but to a lesser degree. Pursuing a somewhat similar line of investigations, Mameli[12] studied the action on alcoholic fermentation of such substances as hydrocarbons, halogen derivatives of hydrocarbons, nitro and nitroso derivatives, amines, alcohols, aldehydes, ketones, acids, phenoxyacetic acid and its salts and cumarone.

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[1] *Chemical Markets,* 20, 23, 867 (1927).

[2] World Trade Notes on Chemicals and Allied Products, 1, No. 16, 3 (1927). See also, *Chemical Markets,* 20, No. 10, 362 (1927).

[3] "Power Alcohol Production," Ministry of Agriculture and Fisheries, England, 1926; see also *Chem. Age* (London), 15, 110 (July 31, 1926).

[4] *Chemicals,* 26, No. 25, 3 (1926).

[5] *Ind. Eng. Chem.,* 19, 46 (1927).

[6] *Paint, Oil and Chemical Review,* 83, No. 10, 13 (1927).

[7] *Planter and Sugar Mfg.,* 77, 29 (1926).

[8] *Chemical Markets,* 20, No. 9, 702 (1927).

[9] U. S. P. 1,599,185 (September 7, 1926).

Flores[13] has patented a method of denaturing ethyl alcohol which comprises adding to the crude alcohol 1% of crude wood alcohol containing acetone and 1% of a light-fraction of mineral oil distilling between 40 and 150°C.

In recent years the attention of various investigators in the United States and elsewhere has been given to a study of methods of preparing substances resembling alcoholic beverages but not conflicting with the prohibition laws. Caspar[14] describes such a method of preparing a dealcoholized beverage. He effects alcoholic fermentation, causing a circulation of the fermenting liquid through the gases and vapors generated by fermentation and condenses the alcohol from the gases and vapors while maintaining the temperature of the liquid at a point less than that at which ebulition occurs. Meyer[15] prepares beer by subjecting a malt-wort extract to a short alcoholic fermentation and producing a sufficiency of acid reaction products during the fermentation to modify the sugar contents of the product as to flavor. The fermentation in the malt-wort extract is stopped by cooling and in the final product clarified away from contact with atmospheric air. Duclaux[16] claims an improved process of clarifying beverages which consists of filtering the fermented liquid through an ultra filter composed of a membrane of nitrocellulose, cellulose acetate, viscose, etc.

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[10] *Intern. Sugar J.*, **28**, 463 (1926).
[11] *Biochem. Z.*, **175**, 135 (1926).
[12] *Brew. Tr. Rev.*, **41**, 63 (1927).
[13] U. S. P. 1,591,084 (July 6, 1926).
[14] U. S. P. 1,598,601 (September 7, 1926).
[15] U. S. P. 1,593,191 (July 20, 1926).
[16] U. S. P. 1,619,016 (March 1, 1927).

Since yeast and ethyl alcohol are jointly produced during the course of the same reaction these two industries are necessarily closely related and have many problems in common. The general principles underlying both processes are the same as far as fermentation is concerned, the chief differences being that the brewer's purpose is to obtain a beverage of good flavor and palatability, while that of the distiller is complete attenuation of the wort and hence utilization of all available carbohydrate. During the course of the past few years the use of yeast as a food and a medicine has been popularized by extensive advertising and at the present time a large amount is utilized in this manner. In Canada the yeast industry has progressed to a point where it is said that yeast has become the main product and alcohol the by-product. Davidson[17] gives an interesting description of the manufacture of yeast and its by-products.

Sherwood and Fulmer[18] describe in considerable detail the results of their study on the effect of temperature on the growth of yeast in various media. With the media which they employed they found that the largest crops were obtained at 42°C., which is higher than the temperature considered optimum for the growth of yeast. Rockwell and Highberger[19] studied the necessity of carbon dioxide for the growth of bacteria, yeasts and moulds. They express the opinion that all of these forms require carbon dioxide for their growth and that the gas is used as a source of carbon. Weldin,[20] in an investigation of the effect of organic acids on the growth of yeast, determined the amounts of the latter required to inhibit the growth of 5 strains of yeast of variable sensitiveness in media of different character. Turner[21] reports the character of 51 cultures of yeast isolated from a number of samples of spoiled carbonated beverages. Rankin[22] found that a governing factor in the rate of fermentation is the quantity of yeast which remains in contact with the liquid during fermentation. The action of the yeast is materially influenced by the various coatings deposited on it. Williams, Wilson and Von der

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[17] *Can. Chem. Met.*, **11**, 90 (1927).
[18] *J. Phys. Chem.*, **30**, 738 (1926).
[19] *J. Infectious Diseases*, **40**, 438 (1927).
[20] *Proc. Iowa Acad. Sci.*, **32**, 95 (1925).
[21] *Proc. Iowa Acad. Sci.*, **32**, 95 (1925).
[22] *J. Inst. Brewing*, **33**, 76 (1927).

Ahe[23] deal with the testing and the concentration of "bios" found in yeast.

Jones[24] describes the method of producing a food product which comprises adding yeast to a mixture of blood and a carbohydrate material, allowing the fermentation to take place and then drying the resulting product. Fiske[25] has patented as a yeast assistant in the making of leavened bread or the like, a product comprising a non-deliquescent dry edible substance and a nitrate dispersed therein. Hildebrandt and Frey[26] describe a method of treating and preparing yeast which comprises causing yeasts to pass into a dormant state by surrounding the cells with a coating having osmotically-acting properties of such strength that it tends so slowly to abstract moisture from the cells that the vitality of the yeast is not destroyed. Mackintosh[27] describes a process for preserving and drying yeast which consists of mixing compressed yeast with a sugar-containing material and heating the mixture so that fermentation is quickly set up, thereby causing rapid drying of the product due to the escape of fermentation gases. Lindemann[28] has patented a process for making fresh yeast lasting, by washing finely distributed fresh yeast in alkaline water maintained at a temperature of 33 to 43°C., until tests show the substantial to complete removal of glycogen.

The success from an industrial point of view of the newest fermentation industry, the butyl alcohol-acetone process, has stimulated continued interest in the various factors relating to the operation of this process and at the same time has shown more clearly the feasibility of still other new processes. The search for new sources of raw material suitable for a particular organism, a problem of prime importance in this branch of the industry as well as in others, has engaged the attention of a number of workers.

Thaysen and Green[29] recommend the use of Jerusalem artichokes as a raw material for the production of butyl alcohol and acetone. When using this material the fermentation is carried out in a mash of 20-30% strength, formed by diluting a 50% mash after hydrolysis of the carbohydrates therein, as by boiling with 0.2% sulfuric acid. Twelve gallons of crude butyl alcohol-acetone mixture may be expected per ton of fresh tubers. The bulk of the carbohydrate is said not to be easily fermentable directly by the organism.

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[23] *J. Am. Chem. Soc.*, **49**, 227 (1927).
[24] U. S. P. 1,599,031 (September 7, 1926).
[25] U. S. P. 1,599,563 (September 14, 1926).
[26] U. S. P. 1,625,121 (April 19, 1927).
[27] U. S. P. 1,596,983 (August 24, 1926).
[28] U. S. P. 1,596,279 (August 17, 1926).
[29] Eng. P. 259,631 (December 8, 1926); see also *J. Inst. Brewing*, **33**, 236 (1927).

Morikawa and Prescott[30] describe what is said to be a new type of organism yielding butyl alcohol and isopropyl alcohol. The yield of alcohols is better in fairly concentrated mashes, that is, those having 12% or more of sugar as glucose, while in solutions of low concentration the yield is relatively low. The organism appears to be very sensitive in the presence of certain salts.

Fred, Peterson and Mulvania[31] have studied the effect of lactic acid bacteria on the butyl alcohol-acetone fermentation. The high-acid forming organisms were found to be most injurious to butyl alcohol fermentation. There is no evidence, however, that lactic acid is more harmful than other organic or inorganic acids. Additions of various acids in amounts sufficient to produce a pH of 4.7 to 4.8 definitely inhibited the growth of the butyl alcohol-acetone forming organism. Studies were made by Hastings, Fred and Carroll[32] on the thermal death point of *Bacillus granulobacter pectinovorum* (the butyl alcohol-acetone organism). They outlined methods of procedure for obtaining consistent results. McCoy, Fred, Peterson and Hastings[33] carried out a very interesting cultural study of the butyl alcohol-acetone organism. Among other interesting data these workers list a great many carbohydrates which the organism ferments and the various products formed. They decided that the slight variations observed between a number of different strains of the butyl organism studied did not warrant separating into different types.

Edmonds[34] describes the process of producing butyl alcohol and acetone in which the fermentation is carried out in at atmosphere of the fermentation gases, whereby contamination of the gases with air is avoided.

The search for new sources of raw material, mentioned above, has extended throughout the vegetable kingdom. Since carbohydrates exist in such large quantity in the form of cellulose the latter would seem to be the ideal raw material and especially so since nature has provided so many agents which act upon cellulose. So far, however, the chief difficulty has been that the fermentations take place rather slowly and in many cases do not go to completion. The present tendency in the utilization of cellulose as a raw material is to first hydrolyze it by chemical means. In this case also the products of hydrolysis are as a rule not fermented with rapidity or completeness,—factors which detract somewhat from the material from a commercial viewpoint. A. W. Schorger in his recent book, "The Chemistry of Cellulose and Wood,"[35] devotes a comprehensive chapter to this subject.

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[30] *J. Bact.*, 13, 58 (1927).
[31] *J. Bact.*, 11, 323 (1926).
[32] *Centralbl. Bakt.*, 2 Abt., 67, 162 (1926).
[33] *J. Infectious Diseases*, 39, 457 (1926).
[34] Eng. P. 268,749 (Filed March 14, 1927).

Langwell[36] describes a process for the fermentation of cellulosic materials according to which the hydrogen ion concentration is maintained within the limits about 10^{-9} and 10^{-5}, measured in the bulk of the mash, by the employment of a compound of an alkali metal (including ammonium) after the addition of a compound of an alkaline earth metal salt (including a salt of calcium or magnesium). Le Franc[37] has patented a process for the manufacture of butyric acid from cellulose. The finely powdered cellulose is hydrolyzed into sugar mash by means of dilute sulfuric acid. The acids produced are neutralized by milk of lime. The sugars are then extracted and fermented by means of bacilli of the type found in garden soil.

Speakman,[38] in a study of fermentation products from cellulose, finds that the utilization of the pentose sugars and galactose by the butyl alcohol-acetone organisms depends on the concentration of the sugar solution and also on the nature and relative porportions of the sugars present in the medium. Peterson, Fred and Marten,[39] in a study of the fermentative powers of the thermophilic microorganism, *Clostridium thermocellum,* found that the products formed from sugars are notably different from those formed from cellulose. Lactic acid is a conspicuous product from the sugars but is not formed from cellulose. Bradley and Rettger[40] discuss various factors which affect the decomposition of cellulose by aerobic bacteria. Koser[41] compares the fermentation of cellobiose by a series of coli-aerogenes cultures with the results of other differential tests used to separate these types.

Interest in other fermentation industries has not been as great as in those which have just been discussed. Pollak[42] describes a continuous process of producing lactic acid from sugar-containing raw materials by means of lactic acid bacteria. Faithfull[43] prepares lactic acid and lactates by fermenting a hydrolyzed carbohydrate with lactic acid bacteria in a slightly acid solution. A gaseous oxidizing material containing free oxygen is introduced during the fermentation in order to retard the production of butyric acid. Pederson, Peterson and Fred[44] found that pure cultures of bacteria may produce dextro- or laevo-lactic acid almost exclusively and that when organisms which do not produce acid are added to the pure cultures, the opposite enantiomorph may be produced. Rogers and Whittier[45] have reported on certain limiting factors in the lactic fermentation. Among other things, they found that holding the pH constant prolongs the fermentation but that it finally ceases; and that reducing the crowding effect by filtering and returning the filtrate does not prolong multiplication or fermentation.

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[35] New York, McGraw-Hill Book Company (1926).
[36] U. S. P. 1,602,306 (October 5, 1926).
[37] U. S. P. 1,625,732 (April 19, 1927).
[38] *Pulp Paper Mag. Can.,* **24**, 731 (1926); *Can. Chem. Met.,* **10**, 229 (1926).
[39] *J. Biol. Chem.,* **70**, 309 (1926).
[40] *J. Bact.,* **13**, 321 (1927).
[41] *J. Infectious Diseases,* **38**, 506 (1926).
[42] U. S. P. 1,624,674 (April 12, 1927).

Several new apparati for use in the fermentation industry have been patented during the past year. Caccia[46] claims a new form of fermentation tube. Vigreux[47] describes an apparatus for the industrial culture of ferments, yeasts, microbes and the like. Matchette[48] describes an apparatus for the propagation of culture germs.

During the past year considerable study has been devoted to the subject of fermentation as applied to the candy industry. Church, Paine and Hamilton[49] came to the conclusion that yeasts tolerant of high percentages of sugar syrup are the cause of the gas evolution which results in the bursting of chocolate-coated creams. Weinzirl[50] expresses the opinion that this phenomenon is caused by anaerobic bacteria, such as possibly *Clost. sporogens, Clost. putrificum* and *Clost. aerofetidum.* Philbrick[51] states that "blown" chocolates usually contain a bacillus which is capable of fermenting glucose under anaerobic conditions.

Baldwin and Fred[52] have recorded the results of a study on the fermentation characters of 60 strains of legume nodule bacteria. The authors found it possible to divide these organisms into two broad groups: (a) the acid producers, and (b) those which lower the hydrogen ion concentration of the culture media.

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[43] Can. P. 270,439 (May 10, 1927). Eng. P. 265,336 (March 30, 1927).
[44] *J. Biol. Chem.*, 68, 151 (1926).
[45] *J. Bact.*, 13, 10 (1927).
[46] U. S. P. 1,614,184 (January 11, 1927).
[47] U. S. P. 1,623,896 (April 5, 1927).
[48] U. S. P. 1,618,461 (February 22, 1927).
[49] *Ind. Eng. Chem.*, 19, 353 (1927).
[50] *J. Bact.*, 13, 203 (1927).
[51] *J. Bact.*, 12, 275 (1926).
[52] *J. Bact.*, 13, 49 (1927).

Varnes[53] and Lawrie[54] describe methods of recovering glycerine from fermented molasses mash.

Cooke[55] describes a fermentation process for transforming organic matter into a form in which its nitrogen is available. The process consists in confining the matter within a chamber, supplying air to the chamber to permeate the matter and maintain and propagate the microorganisms peculiar to fermentation and regulating the temperature of the air in accordance with fermentation requirements.

In the fermentation processes most extensively in use at the present time a large proportion of the raw material is consumed in the production of gaseous by-products. In the production of ethyl alcohol this amounts to about 36%, in the form of carbon dioxide. In the butyl alcohol-acetone industry, each 100 pounds of starch yields about 60% of carbon dioxide and 1.6% of hydrogen. When the daily consumption of raw materials at these plants is considered it will be seen that immense quantities of these products are available. Suitable utilization of these by-products would serve to materially lower the production costs of the main products. During the past year a plant was put into operation by one of the large fermentation companies to utilize the hydrogen produced in its process for the manufacture of ammonia. Later this plant was converted over to the manufacture of synthetic methanol, and is now producing a substantial portion of this country's requirements from the mixture of hydrogen and carbon dioxide produced in the fermentation process. The absence of substances which ordinarily act as catalyst poisons makes this gaseous mixture particularly adapted for this purpose. Commercially feasible processes for the utilization of the large quantities of carbon dioxide now going to waste will mark another important step forward. At present the Dry Ice industry and the use of carbon dioxide as a plant food in green-houses seem to offer possibly the best opportunities for solving this important problem. The freedom of fermentation gases from sulfur and other similar obnoxious substances makes them better suited for plant food than any hitherto available.

[53] U. S. P. 1,626,986 (May 3, 1927).
[54] U. S. P. 1,627,040 (May 3, 1927).
[55] U. S. P. 1,597,724-5 (August 31, 1926).

Chapter XXXVIII.

Pharmaceutical Chemistry.

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For ease of reference a number of subheads are used in this year's survey of progress, and again there will undoubtedly be some duplication of reports on subjects which may be also properly mentioned in other chapters. More complete references to patents are given than last year, and even though they may be based on foreign work, a number are mentioned for the reason that the granting of a U. S. or Canadian patent may strongly influence research in America on the same subject.

Plants and Vegetable Drugs. As a result of interest aroused in the alkaloids and medicinal properties of *Ephedra vulgaris,* or what now appears to be preferably known as "*Ephedra Sinica,*"[1] there have appeared during the past year quite a number of papers concerning this and related species. Chen and Kao[2] record some new work, and give a very full summary of their previous work and a most complete bibliography of all previous records. Masucci and Suto,[3] and Schoetzow and Needham[4] make note of investigation of the ephedrine content of the drug. Tsiang and Brown[5] report work on the isolation and detection of ephedrine from the toxicological standpoint. Nielsen, McCausland and Spruth[6] have investigated the occurrence and alkaloidal content of a number of species of *Ephedra,* and Terry[7] reports no ephedrine in *E. Nevadensis.*

Digitalis receives its customary attention at the hands of several investigators. Methods of standardization largely physiological, and factors influencing results, are the subject of researches by Berardi,[8] Haag,[9] and by Knafflenz,[10] who supplies also in his paper a very useful bibliography of some 135 other papers. Konnerth and Pickering[11] compare *Digitalis lutea* and *D. purpurea,* while Sparks[12] has investigated digitalis from British Columbia, Rowe[13] reports extensive experimental work with a colorimetric assay, and Macht and Krantz[14] study a method based on phyto-pharmacological reactions. The same investigators[15] report a study of the deterioration of digitalis preparations caused by ultraviolet radiation and by polarized light.[16]

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[1] Farwell, *J. Am. Pharm. Assoc.,* **16**, 135 (1927).
[2] *J. Am. Pharm. Assoc.,* **15**, 625 (1926).
[3] *J. Am. Pharm. Assoc.,* **15**, 748 (1926).
[4] *J. Am. Pharm. Assoc.,* **15**, 1070 (1926).
[5] *J. Am. Pharm. Assoc.,* **16**, 294 (1927).
[6] *J. Am. Pharm. Assoc.,* **16**, 288 (1927).
[7] *J. Am. Pharm. Assoc.,* **16**, 397 (1927).

On the subject of drugs containing anthraquinone derivatives, particularly cascara, Tumminkatti and Beal[17] continue the extensive investigation that Beal and various coworkers have had in progress for several years, endeavoring to find a reliable method for quantitative evaluation, but so far without satisfactory conclusion. Peacock and Peacock[18] report that they have proved the absence of tannin from cascara.

Colin[19] describes the production of active extracts from the plant *Tecoma mollis,* and tests of same indicating anti-diabetic qualities. *Ceanothus americanus* is further studied this year in an endeavor to elucidate its action as a blood coagulant by Thoraldsen and Krawitz[20] and J. T. Groot.[21] Extensive work on Philippine ginger and its constituents is reported by Valenzuela.[22] Chen[23] has obtained from *Illicium religiosum* a crystallizable toxic substance and a toxic volatile oil, but for neither is there yet suggested a specific therapeutic use. Githens[24] describes certain work on constituents of Miré. The constituents of several species of the genus Mentha have been extensively studied by Gordon,[25] and the volatile oil of *Asaurum caudatum* is the subject of careful investigation by Burlage and Lynn.[26]

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[8] *J. Am. Pharm. Assoc.,* **15**, 563 (1926).
[9] *J. Am. Pharm. Assoc.,* **16**, 516 (1927).
[10] *J. Pharmacol.,* **29**, 407 (1926).
[11] *J. Am. Pharm. Assoc.,* **15**, 1069 (1926).
[12] *J. Am. Pharm. Assoc.,* **16**, 203 (1927).
[13] *J. Am. Pharm. Assoc.,* **16**, 510 (1927).
[14] *J. Am. Pharm. Assoc.,* **16**, 210 (1927).
[15] *Proc. Soc. Exptl. Biol. Med.,* **23**, 340 (1926).
[16] *J. Am. Pharm. Assoc.,* **16**, 106 (1927).
[17] *J. Am. Pharm. Assoc.,* **15**, 847 (1926).
[18] *J. Am. Pharm. Assoc.,* **15**, 639 (1926).
[19] *J. Am. Pharm. Assoc.,* **15**, 556 (1926); **16**, 199 (1927).
[20] *Am. J. Physiol.,* **79**, 545 (1927).
[21] *J. Pharmacol.,* **30**, 275 (1927).
[22] *J. Am. Pharm. Assoc.,* **15**, 652, 734 (1926).
[23] *J. Am. Pharm. Assoc.,* **15**, 861 (1926).
[24] *J. Am. Pharm. Assoc.,* **15**, 1067 (1927).
[25] *J. Am. Pharm. Assoc.,* **16**, 130 (1927).
[26] *J. Am. Pharm. Assoc.,* **16**, 407 (1927).

Swanson and Hargreaves[27] report upon the standardization of aconite preparations, and particularly the effect of H ion concentration on stability. Davy and Chu[28] present a further study of the glucosides of *Caulophyllum thalictroides* and especially the effect of enzymes in the drug upon the glucosides as extracted, while Melanoff and Schaefer[29] add some data to our information regarding the resin of *Podophyllum peltatum.*

Alkaloids. Several researches pertaining to alkaloids are included by preference in the preceding sections. In reviewing the literature for the year on alkaloids it is noteworthy that by far the greater portion, especially work on the constitution of the alkaloids and their derivatives, emanates from European sources. This is a branch of chemical investigation that is apparently receiving but little attention in the United States, perhaps because of the greater attractiveness of many other branches of medicinal chemistry.

Quinine and quinidine are studied as regards toxicity, mode of elimination, and methods of detection by Weiss and Hatcher,[30] and by Hatcher and Gold.[31] The stability of atropine and hyoscyamine under various conditions associated with methods of analysis is determined by Palkin and Watkins[32] and the relation of pH value to the stability of physostigmine solutions is reported by Krantz and Slama.[33]

Oils. Contributions to the chemistry of medicinal oils were quite limited. A number of new esters of chaulmoogric acid were prepared by Herrera-Batteke and West,[34] while Perkins and Cruz[35] have synthesized *dl*-chaulmoogric acid. Dubin[36] indicates lack of efficiency of the colorimetric method of determining vitamin content of cod liver oil as compared to the biological method. Funk and Dubin[37] have patented a concentrate from cod liver oil containing both anti-xerophthalmic and anti-rachitic vitamins and process of making same.

Metallic Compounds. Little of interest can be recorded under this head except as pertains to organo-metallic compounds, and though these are covered in a separate chapter, because of interest from the medicinal standpoint a list of patents is given at the end of this section, including also those which, though U. S. Patents, may not have been the result of researches in America.

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[27] *J. Am. Pharm. Assoc.,* **16**, 296 (1927).
[28] *J. Am. Pharm. Assoc.,* **16**, 302 (1927).
[29] *Am. J. Pharm.,* **99**, 323.
[30] *J. Pharmacol.,* **30**, 327, 335 (1927).
[31] *J. Pharmacol.,* **30**, 347 (1927).
[32] *J. Am. Pharm. Assoc.,* **16**, 21 (1927).
[33] *J. Am. Pharm. Assoc.,* **16**, 412 (1927).
[34] *Philippine J. Sci.,* 31, 161 (1926).
[35] *J. Am. Chem. Soc.,* **49**, 1070 (1927).
[36] *J. Am. Pharm. Assoc.,* **16**, 41 (1927).
[37] U. S. P. No. 1,629,074 (May 17, 1927).

Broady and Jordan[38] describe the production of ointments of metallic substances in colloidal form, especially silver, mercury and mercurous chloride. Because of possible interest from the medical viewpoint, the work of Browne and Reid[39] on reactions of lead tetraethyl may be mentioned here.

U. S. Patents. 1,604,143 (Bockmühl and Ludwig, Oct. 26, 1926), bismuth compounds of aminophenols; 1,605,691 (Raiziss and Kremens, Nov. 2, 1926), arseno-bismuth compounds; 1,607,196 (Hahl and Kropp, Nov. 16, 1926), vanadium compounds of 8-hydroxy-quinoline as spirocheticides; 1,610,391 (Smith, Dec. 14, 1926), colloidal silver iodide-protein compound; 1,613,569 (Sagi, Jan. 4, 1927), mercury derivatives of hydroxysulfo-benzoic acid; 1,615,226 (Lapenta and Reisler, Jan. 25, 1927), on medicinal preparations of colloidal bismuth; 1,616,204 (Streitwolf and Hallensleben, Feb. 1, 1927), various complex metallic arsenobenzene compounds; 1,616,365 (Hahl, Feb. 1, 1927), medicinal compounds of antimony oxide with salts of hydroxyquinoline sulfonic acids; 1,616,366 (Hahl, Feb. 1, 1927), complex antimony compounds of thioglycollic acid; 1,618,172 (Crossley, Feb. 22, 1927), a magnesium salt of 2-phenylquinoline-4-carboxylic acid; 1,621,121 (Lowy, Mar. 15, 1927), medicinal preparations of arsphenamine; 1,621,757 (Seydel, Mar. 22, 1927), the use of calcium benzylsuccinate as an anti-spasmodic, and for treatment of high blood pressure. This appears to be a case of patenting a substance for a particular use.

Synthetic Organic Products. Only very limited reference will be made here to published results of researches but a number of patents of interest from the medicinal viewpoint are listed as briefly as possible.

Orndorff and various associates continue work on phthaleins and related or derived substances, many of which in the past have proved medicinally interesting as may some of these newer derivatives; see extensive studies by Orndorff, Gibbs and McNulty,[40] Orndorff and Fuchs,[41] Orndorff and Lacey,[42] thymolbenzein and

[38] *J. Am. Pharm. Assoc.,* **16**, 425 (1927).
[39] *J. Am. Chem. Soc.,* **49**, 830 (1927).
[40] *J. Am. Chem. Soc.,* **48**, 1994 (1926).
[41] *J. Am. Chem. Soc.,* **48**, 1939 (1926).
[42] *J. Am. Chem. Soc.,* **49**, 818 (1927).

certain benzophenone derivatives; and Orndorff and McNulty,[43] *o*-cresolbenzein and some derivatives. Thymoltetrachlorphthalein and derivatives have been studied by Cornwell and Esselstyn.[44]

Renshaw and Hotchkiss[45] present the results of work on betaine derivatives as a continuation of a study of the basis for physiological action of -onium compounds.

The chemical constitution of local anesthetics as related to H ion concentration is the subject of investigation by Vliet and Adams.[46] Hargreaves[47] describes the preparation of quinoline-*o*-quinone and its relation to the thalleioquin reaction, while in the field of biochemistry Dudley, Rosenheim and Starling[48] present further studies on the structure and synthesis of spermine. Related to recent investigations of thyroxin is that of West[49] on the influence of some diiodotyrosine derivatives on basal metabolism. The relaxing or antispasmodic action of some aromatic esters is shown by Lynn and Gaston.[50] As a result of difficulty in identifying constituents of peppermint Gordon and Kremers[51] present some investigation and suggested revision of the pentanols.

Puntambeker and Adams[52] add to our knowledge of the polyhydroxyanthraquinones by describing the synthesis of hydroxyanthrarufin and rufiopin.

U. S. Patents. 1,596,259 (Thayer, Aug. 17, 1926), picrates of local anesthetics including *n*-butyl-*p*-aminobenzoate, ethyl-*p*-aminobenzoate, methyl-*m*-amino-*p*-hydroxybenzoic acid, diethylaminoethyl-*p*-aminobenzoate (procaine), and di-*n*-butylaminopropyl-*p*-aminobenzoate; 1,604,472 (Nightingale, Oct. 26, 1926), process of making acetylsalicylic acid; 1,606,171 (Mills, Nov. 9, 1926), method of making salol and other aryl esters; 1,606,624 (Fourneau and Trefouel, Nov. 9, 1926), a symmetrical ureide of sodium *m*-aminobenzoyl-*m*-amino-*p*-methylbenzoyl-1-naphthylamino-4,6,8-trisulfonate, a trypanosomicide; 1,609,520 (Layraud, Dec. 7, 1926), *CC*-*n*-butylethylbarbituric acid, a hypnotic; 1,612,598 (Anderson, Dec. 28, 1926), sugar derivatives of 3,3-diamino-4,4-dihydroxyarsenobenzene; 1,611,978 (Wolffenstein, Dec. 28, 1926), esters of terpene alcohols, especially menthyl and bornyl, nicotinate and picolinate; 1,614,281 (Churchman, Jan. 11, 1927), a germicide for both gram-positive and gram-negative bacteria comprising a basic triphenylmethane dye, such as gentian violet, and a neutral acridine dye such as acriflavine; 1,615,870 (Dox, Feb. 1, 1927), secondary butyl-allyl-barbituric acid; 1,615,989 (MacEwen, Feb. 1, 1927), solutions of arsphenamine and similar compounds with dextrose and Na_2PO_2 as preservatives; 1,616,109 (Bunbury, Feb. 1, 1927), aminodianthrimides; 1,616,144 (Schoeller and Gehrke, Feb. 1, 1927), a symmetrical ureide of *p*-hydroxy-*m*-aminobenzenearsonic acid; 1,616,282 (Schranz and Lutter, Feb. 1, 1927), 1-methoxymethyl-3,7-dimethylxanthine, similar in action to caffeine; 1,616,533 (Krause and Róka, Feb. 8, 1927), the production of formaldehyde from methylene chloride; 1,621,094 (Volwiler, Mar. 15, 1927), a derivative of butylethylbarbituric acid by reaction with diethylamine; 1,622,129 (Boedecker, Mar. 22, 1927), substituted barbituric acids containing a halogenallyl group; 1,622,271 (Benda, Mar. 29, 1927), 3-chloro-4-hydroxy-5-acetylaminophenylarsine oxide, a preparation for destruction of spirochetes; 1,623,949 (Gubelmann, Weiland and Stallmann, Apr. 5, 1927), the production of guiacol from diazo-*o*-anisole; 1,624,546 (Dox, Apr. 12, 1927), ethylhexylbarbituric acid; 1,624,675 (Preiswerk, Apr. 12, 1927), diacetyldiphenolisatin for use as a laxative; 1,625,771 (Schoellkopf, Apr. 12, 1927), a method for production of menthol from thymol.

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[43] *J. Am. Chem. Soc.*, 49, 992 (1927).
[44] *J. Am. Chem. Soc.*, 49, 826 (1927).
[45] *J. Am. Chem. Soc.*, 48, 2698 (1926).
[46] *J. Am. Chem. Soc.*, 48, 2158 (1926).
[47] *J. Am. Pharm. Assoc.*, 15, 750 (1926).
[48] *Biochem. J.*, 20, 1082 (1926).
[49] *Proc. Soc. Exptl. Biol. Med.*, 23, 629 (1926).
[50] *J. Am. Pharm. Assoc.*, 15, 560 (1926).
[51] *J. Am. Pharm. Assoc.*, 16, 222, 313, 419 (1927).
[52] *J. Am. Chem. Soc.*, 49, 486 (1927).

Gland Products. In spite of the great interest in the endocrine glands and the large amount of investigation going on, relatively little has been published. Heyl and Fullerton[53] continue the chemical examination of ovarian residue and submit data relative to the water soluble, alcohol insoluble, nitrogenous extracts. From a study of the depressor action of liver extracts Burnett[54] concludes that histamine, probably combined with other substances, is the substance responsible for this action. It is reported by Funk[55] that by what is described as a "mild fractionation procedure" he has obtained from insulin two substances of quite different effects on the sugar content of the blood, one causing the usual reductions of blood sugar, but the other bringing about an increase of blood sugar and great dilution of the blood by retention of water.

Digestive Ferments. Nothing particularly new has been reported. Tests on the effect of excessive acidity on the activity of

[53] *J. Am. Pharm. Assoc.*, **15**, 549 (1926).
[54] *Am. J. Physiol.*, **78**, 449 (1926).
[55] *Science*, **65**, 39 (1927).

dry pepsin are described by Dinger and Honsinger[56] and Waksman[57] has obtained a patent on proteolytic enzymes from *Aspergillus flavus*.

Pharmaceutical Analysis. Of interest from the analytical viewpoint, work as cited below may be mentioned:

A study of test reactions for diethyl phthalate by Handy and Hoyt[58] and by Scott and Will;[59] a method of analysis of mixtures of cod liver oil and malt extract by Waggoner and Glover;[60] new color reactions for various local anesthetics, especially procaine, by Riegel and Williams.[61] Pertaining to the mydriatic alkaloids, Watkins and Palkin[62] direct attention to errors of analysis due to presence of fatty acids; Edwards and Schoetzow[63] comment on methods of avoiding low results on tablets of atropine sulphate, as does also Stikarofsky[64] on hyoscyamus preparations.

From the laboratory of the A. M. A. comes a report of chemical examination of ethylene for anesthesia.[65] A possible colorimetric method for the assay of strophanthus is reported by Rowe[66] as of fair accuracy but of no use for squill, convallaria, or veratrum. An attempt to adapt to standards for determination of pH concentration the stable colored solutions of Co—Fe—Cu, advocated as color standards by Arny, is made by Taub,[67] who describes methods of preparing and tests on seventy-three permanent standards covering a pH range of 1.2 to 9.0.

An accurate method for determination of bismuth in tissues, excreta, blood and bone, of special use in studies of physiological action of bismuth compounds, is described by Sultzaberger.[68] Carswell[69] determines that differences of melting points of various lots of acetylsalicylic acid are due to difference in crystal structure, and are not shown by finely powdered material.

General Information. Owing to the necessity for much earlier preparation of material for this volume than for that of 1926, there is no new report of the Council on Pharmaceutical Research presided over by Dr. H. V. Arny, to which reference can be made. While not fully up to date, special reference should be made to the very complete survey of chemotherapeutic researches by Bogert.[70] This list of researches in progress is helpful and suggestive, and of such a nature that it will not quickly become out of date.

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[56] *J. Am. Pharm. Assoc.*, **15**, 866 (1926).
[57] U. S. P. No. 1,611,700 (Dec. 21, 1926).
[58] *J. Am. Pharm. Assoc.*, **16**, 7 (1927).
[59] *J. Am. Pharm. Assoc.*, **16**, 417 (1927).
[60] *J. Am. Pharm. Assoc.*, **15**, 754 (1926).
[61] *J. Am. Chem. Soc.*, **48**, 2871 (1926).
[62] *J. Assoc. Official Agr. Chem.*, **10**, 130 (1927).
[63] *J. Am. Pharm. Assoc.*, **15**, 967 (1926).
[64] *J. Am. Pharm. Assoc.*, **16**, 30 (1927).
[65] *J. Am. Med. Assoc.*, **88**, 322 (1927).
[66] *J. Am. Pharm. Assoc.*, **16**, 113 (1927).
[67] *J. Am. Pharm. Assoc.*, **16**, 116 (1927).
[68] *J. Am. Pharm. Assoc.*, **16**, 218 (1927).
[69] *J. Am. Pharm. Assoc.*, **16**, 306 (1927).

It seems scarcely necessary to append to this year's report a suggested list of important research problems, as it would be either identical with or an elaboration of the one given very briefly last year.

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[70] *J. Am. Pharm. Assoc.*, **16**, 123 (1927).

Chapter XXXIX.

Glass.

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The past few years have seen a great advance in our knowledge of the fundamental chemistry of glass, especially at high temperatures. Little work has been done in America on the properties of glass at ordinary temperatures, but mention should be made of the work in England prior to 1925, some of which has been continued. This includes the comprehensive work of Peddle[1] on Na_2O, K_2O, and mixed Na_2O—K_2O glasses containing CaO, BaO or PbO and SiO_2, and of Turner and his co-workers.[2] Bridgman[3] measured the compressibility of SiO_2 glass, Pyrex, two other highly siliceous glasses and an alkali-aluminum borate glass free from SiO_2, as well as some natural glasses. The SiO_2-free glass showed the normal decrease in compressibility with increasing pressure, while the siliceous glasses showed an increase in compressibility with pressure, which was greatest with SiO_2 glass.

An important contribution to the study of the tensile strength of glass has been made by Littleton,[4] which minimizes the tendency toward low results because of surface cracks. Since glass is much stronger in compression than in tension, a chilled specimen, whose surface is under strong compression, will tend to fracture under load in its interior. By combining graphically the original stress, as determined from the strain pattern, with the load stresses, the actual tensile strength of the glass can be obtained.

Of particular interest in the technology of glass are the papers by Gage[5] on "Colored Glass for Stage Illumination" and by Littleton and Shaver[6] on the relative temperatures of Pyrex and porcelain in sunlight, in the second of which it was shown that the temperature of porcelain insulators increases on the average about three and one-half times that of a Pyrex glass insulator. McCauley [7] has discussed the flow of heat through molten glass and through furnace walls, and determined the thermal conductivity of flux blocks and the apparent conductivity of glass as a function of temperature. Littleton and Bates [8] have studied the relative efficiency of Pyrex glass and metal condenser tubes, and find that because of the controlling influence of the surface film resistance the difference in condensation between metal and glass tubes is far less than would be expected from the difference in conductivity.

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[1] *J. Soc. Glass Tech.*, **4** (1920) to **7** (1923).

[2] *J. Soc. Tech.*, **4** (1920) to **10** (1926).

[3] *Am. J. Sci.*, **10**, 359 (1925).

[4] *Phys. Rev.*, **22**, 510 (1923).

[5] *Trans. Soc. Motion Picture Eng.*, May, 1924, p. 37.

[6] *J. Am. Ceram. Soc.*, **9**, 618 (1926).

The electrolysis of glass has interested several workers. Rebbeck and Ferguson [9] studied the evolution of gas and its relation to sorption and conductivity, and concluded that the gas formed on electrolysis, using a Hg cathode, came from the adsorbed water, not by direct electrolysis but by a secondary reaction with sodium ions from the glass. The conductivity of the glass was not dependent on absorbed water. Further studies by Rebbeck, Mulligan and Ferguson [10] showed that the resistance was increased by heat treatment above 300°, the effect being caused chiefly by a decrease in the speed of the ions, to a less degree by a change in the number of carriers. The electrolysis of glass has also been studied by Burt,[11] and by Hurd, Engel and Vernon.[12] The latter author studied the electrolytic replacement of sodium in glass by other alkali metals and by ammonium. Sodium can be replaced by sodium with but little effect on the glass; ammonium ions replace sodium with less effect than other ions, but cause fracture if introduced in sufficient quantity; and silver, potassium and lithium were, in the order given, less able to make a substitution.

Dennis,[13] and Dennis and Laubengayer [14] prepared glasses in which the SiO_2 is replaced by GeO_2. In a flint of $n_D = 1.967$, one of $n_D = 1.644$, a borate crown of $n_D = 1.517$, and a barium crown of $n_D = 1.573$ the SiO_2 was replaced by an equimolecular amount of GeO_2, and the resulting glasses had n_D of 2.068, 1.794, 1.619, and 1.670 respectively. The GeO_2 glasses were more easily

[7] *J. Am. Ceram. Soc.*, **8**, 493 (1925).
[8] *Trans. Am. Inst. Chem. Eng.*, **17**, 95 (1925).
[9] *J. Am. Chem. Soc.*, **46**, 1991 (1924).
[10] *J. Am. Ceram. Soc.*, **8**, 329 (1925).
[11] *J. Optical Soc. Am.*, **11**, 87 (1925).
[12] *J. Am. Chem. Soc.*, **49**, 447 (1927).
[13] U. S. P. 1,607,817 (Nov. 23, 1926).
[14] *J. Phys. Chem.*, **30**, 1510 (1926).

melted and fined than the corresponding SiO_2 glasses. Taylor[15] has patented a SiO_2-free glass containing 50-67% Al_2O_3, 5-20% CaO or other oxide of a second group element and not over 10% of alkali, of which over one-half is K_2O.

A most interesting development is the new glass transmitting practically all the ultra-violet that is transmitted by the atmosphere, announced by Hood.[16] The density of the new glass is 2.64, $n_D = 1.539$, $n_F - n_C = 0.009$. The transmission at 290 mμ, the extreme limit of the sun's rays through the atmosphere, was 86% through 2 mm. (uncorrected for surface reflection).

An important series of papers has appeared from the Bureau of Standards dealing with the properties of glass in the annealing range, and the effect of heat treatment in this range on the properties of the treated glass. The first of these papers appeared in 1920: that of Tool and Valasek,[17] "Concerning the annealing and characteristics of glass," in which it was shown that at or slightly above the temperature at which strain in glass was observed to disappear rapidly when using an optical method there is a marked evolution of heat on cooling, and an adsorption of heat on heating. It was later found by Tool and Eichlin[18] that these exothermic and endothermic effects were dependent on the previous thermal history of the sample, the relationship between the two in some cases being comparatively simple, but in others not so evident. Peters and Cragoe[19] showed that a marked change in the thermal dilatation of glass takes place in the same temperature region. Observations were made from 20 to 650°C. on 32 kinds of glass, the compositions of most of which were known, either by calculation from the batch, or by analysis. The observed dimensional changes are represented by curves which show that the glasses pass through a critical expansion region, in which the expansion rate increases by 2 to 7 times. This critical region, which for any one glass does not exceed 40°, was found as low as 400° with a lead tubing and a fusing-in glass, both of unknown composition, and as high as 575°C. with a barium crown containing 47.6% SiO_2, 4% B_2O_3, 6% K_2O, 2% Na_2O, 9.9% ZnO, and 29.2% BaO. About 75° above the critical region the glass softens and contracts. Peters[20] later studied the refractive index, as well as thermal expansion, using 9 different samples, mostly of known composition, from 20-700°C. The index of refraction increased in the critical expansion region, then decreased in the rapid expansion region, and increased again above the softening temperature. While it was to be expected that the index would decrease with the density, in every case the measured index was much larger than the index computed from the relation $\frac{n-1}{d} = C$.

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[15] U. S. P. 1,609,329 (Dec. 7, 1926).
[16] *Science,* 64, 281 (1926).
[17] Bur. Stand., Sci. Paper No. 358 (1920).
[18] *J. Am. Ceram. Soc.,* 8, 1 (1925).
[19] Bur. Stand., Sci. Paper No. 393 (1920).
[20] Bur. Stand., Sci. Paper No. 521 (1926).

Further studies by Tool and Eichlin[21] and Tool and Hill[22] have shown that the properties of glass at room temperature are dependent on their thermal history, especially on the temperature and duration of annealing or heat treatment. The density and index of a glass may be increased by heat treatment at a lower temperature than that to which it has previously been subjected, or decreased by treatment at higher temperature. The index and density can be altered at will by appropriate choice of temperature and duration of heating, the change in density often exceeding 1%. It should be emphasized that the effect under consideration is not to be ascribed to strain, which was absent, but to changes in the glass itself. These changes take place rapidly at the higher temperatures, in the neighborhood of the "upper annealing temperature," more slowly at lower temperature.

The preceding papers have dealt with the properties of glass in the annealing range, and the determination of annealing temperatures by thermal and dilatation measurements. Finn[23] has discussed the annealing of glass from a practical as well as theoretical standpoint, and Preston[24] has derived by dimensional analysis the formula used by Adams and Williamson[25] in their fundamental discussion of glass annealing.

The melting point diagram of the ternary system Na_2SiO_3—$CaSiO_3$—SiO_2, determined by Morey and Bowen,[26] is reproduced in Fig. 1. On it are the fields of the compounds $CaO.SiO_2$, $Na_2O.2CaO.3SiO_2$, $2Na_2O.CaO.3SiO_2$, $Na_2O.SiO_2$, $Na_2O.2SiO_2$, $Na_2O.3CaO.6SiO_2$, and the three forms of SiO_2, quartz, tridymite and cristobalite. Of the ternary compounds, $Na_2O.2CaO.3SiO_2$ is the only one with a congruent melting point, and it is characterized by an unusually flat melting point surface, indicative of great dissociation on melting. In this respect it resembles $Na_2O.2SiO_2$. The other ternary compounds, $2Na_2O.CaO.3SiO_2$ and $Na_2O.3CaO.6SiO_2$, are decomposed before their melting points, and the field of stability of the latter compound is far from the point representing its composition. In the region in which it crystallizes from the melt it is probable that it exists in but small degree, and the fact that glasses in which it is the primary phase are difficult to crystallize may be associated with this extreme dissociation. The ternary eutectic, $Na_2O.2SiO_2$—$Na_2O.3CaO.6SiO_2$—quartz, at 725°, is the lowest melting mixture in the system, and mixtures near to it in composition are extraordinarily difficult to crystallize. The ordinary soda-lime glass of commerce consists essentially of this eutectic, modified in composition by the addition of small amounts of some or all of the oxides, CaO, MgO, Al_2O_3 or SiO_2, to increase the chemical stability, and the fact that glasses can be worked without devitrification is explained by the low temperature of this eutectic. At the temperatures at which glass is melted

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[21] *J. Optical Soc. Am.*, **8**, 419 (1924).
[22] *J. Soc. Glass Tech.*, **9**, 185 (1925).
[23] *J. Am. Ceram. Soc.*, **9**, 493 (1926).
[24] *Trans. Optical Soc.*, **26**, 14 (1924-5).
[25] *J. Franklin Inst.*, **190**, 597, 835 (1920).
[26] *J. Soc. Glass Tech.*, **9**, 226 (1925).

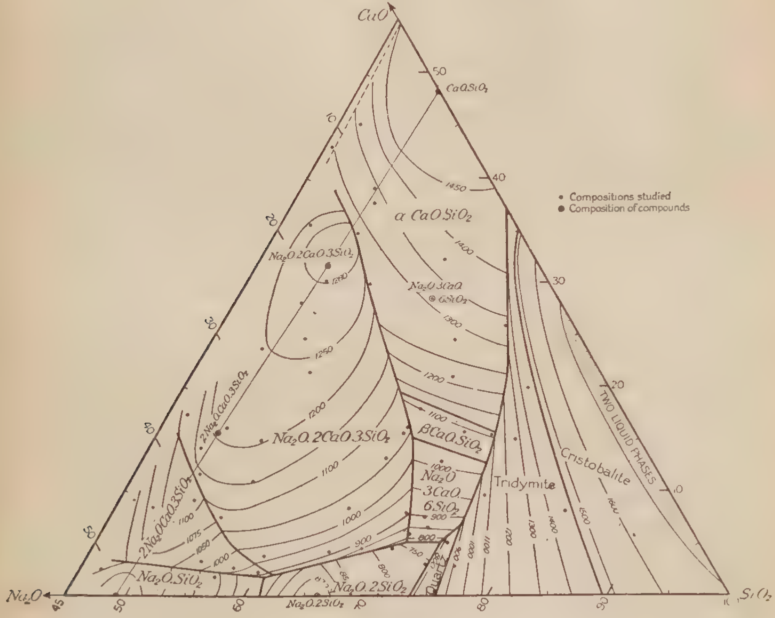

FIG. 1.

and worked, it is well above its freezing point, and at the temperature at which devitrification should begin the high viscosity, and the characteristic reluctance to crystallize of the primary phases, are sufficient to prevent crystallization in the ordinary course of procedure.

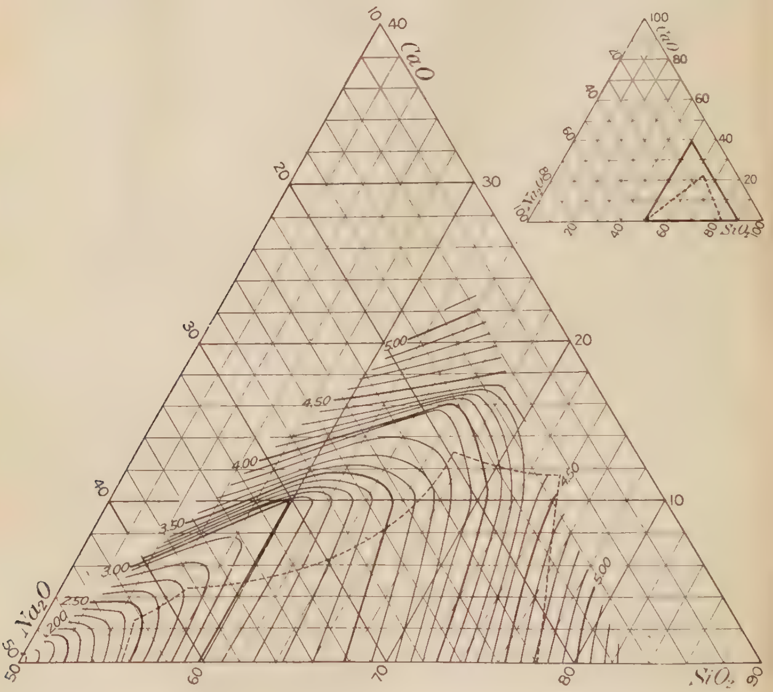

FIG. 2.

An attempt by Wyckoff and Morey [27] to gain information as to the constitution of glass by X-ray methods gave no conclusive results. In the composition region surrounding the ternary $Na_2O.2SiO_2$—$Na_2O.3CaO.6SiO_2$– quartz eutectic and the stability field of $Na_2O.3CaO.6SiO_2$, broad patterns of the type called liquid patterns were obtained, while other parts of the field gave line patterns. But little correlation could be observed between the type of X-ray pattern and the melting point diagram. In a later paper the same authors[28] establish a structure for the compound $Na_2O.CaO.SiO_2$, and give X-ray data for other compounds in the system. They found, however, that the pattern which is obtained from a glass, even though it be of the composition of a pure crystal, is not the same as that from the crystal itself, and the explanation of the line patterns obtained from glasses is still an open question.

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[27] *J. Soc. Glass Tech.*, 9, 256 (1925).

Another research which should be mentioned is that of Washburn, Shelton and Libman[29] on the viscosity and surface tension of the soda-lime glasses. Viscosities were determined by the rotating cylinder method in an apparatus calibrated with glucose and glucose-dextrose syrups, whose viscosities had been determined with the Ostwald viscosimeter, the falling sphere method, and the rate of flow through a capillary tube. Measurements were made on the 16 glasses whose compositions are given in Table 1. These glasses were made up by mixing the analyzed glasses 1, 2, and 5. The relation between temperature and the logarithm of viscosity is summarized in the interpolated values of Table 2. Figure 2 gives values of the lines of equal viscosity at 1000°, and on the same figure is reproduced the freezing point curve for 1000°, from the work of Morey and Bowen, to illustrate the lack of correlation between the two. The viscosity of soda-lime glasses has also been studied in England by English[30] and by Stott,[31] and the results of all these observers discussed by Fulcher.[32]

Table 1. Composition of Various Glasses

Glass	Percentage composition			Glass	Percentage composition		
No.	SiO_2	Na_2O	CaO	No.	SiO_2	Na_2O	CaO
1	49.7	50.3	...	9	54.25	38.0	7.75
2	82.6	17.4	...	10	70.0	10.0	20.0
3	70.0	30.0	...	12	72.25	15.1	12.1
4	60.0	40.0	...	13	73.5	16.5	10.0
5	63.0	13.6	23.4	14	73.0	12.0	15.0
6	60.5	20.0	19.5	15	67.5	15.5	17.0
7	68.1	21.9	10.0	16	64.95	19.3	15.75
8	70.0	20.0	10.0	17	60.0	30.0	10.0

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[28] *Am. J. Sci.*, **12**, 419 (1926).

[29] Univ. of Ill., Bull. No. 140 (1924).

[30] *J. Soc. Glass Tech.*, **7**, 25 (1923); **8**, 205 (1924); **9**, 83 (1925); **10**, 52 (1926).

[31] *J. Soc. Glass Tech.*, **9**, 207 (1925); **10**, 424 (1926). *Proc. Roy. Soc.*, **108A**, 154 (1925); **112A**, 499 (1926).

[32] *J. Am. Ceram. Soc.*, **8**, 339, 789 (1925).

Table 2. Logarithm Viscosity (log η) at Temperature:

Glass No.	1500°	1400°	1300°	1200°	1100°	1000°	900°	800°
1	....	....	....	0.93	1.167	1.620	2.320	....
2	2.330	2.638	3.070	3.690	4.500	5.4	....	....
3	1.580	1.887	2.205	2.620	3.104	3.640	4.300	5.140
4	0.91	1.257	1.630	2.050	2.500	3.040	3.683	4.515
5	1.19	1.510	1.913	2.630	3.770	5.165	....	....
6	0.93	1.323	1.708	2.143	3.53	4.95	....	....
7	1.441	1.800	2.160	2.587	3.140	3.765	4.445	5.185
8	1.580	1.940	2.330	2.777	3.306	3.930	4.685	5.630
9	....	0.88	1.230	1.645	2.130	3.415	(6.05)	....
10	1.770	2.160	2.640	3.840	5.79	....	....	....
12	1.627	2.090	2.560	3.030	3.590	4.365	5.460	....
13	1.680	2.180	2.700	3.260	3.850	4.460	5.090	5.73
14	2.43	2.805	3.190	3.710	4.8	....	....	....
15	1.57	1.910	3.320	2.890	3.555	4.370	5.500	....
16	1.41	1.750	2.120	2.580	3.150	3.880	4.920	....
17	1.08	1.445	1.805	2.180	2.580	3.02	(3.5)	....

The surface tension measurements of Washburn, Shelton and Libman, made by measuring the pull on a vertical ring, are summarized in Table 3. Here again there is no correlation between the properties of the liquid and the melting point surface.

Table 3. Surface Tension of Various Glasses

Glass No.	Surface tension (dynes per cm.) at		Glass No.	Surface tension (dynes per cm.) at	
	1206°	1454°		1206°	1454°
2	....	153.7	9	165.4	153.7
3	164.0	148.8	10	164.0	156.4
4	156.1	153.6	12	....	151.6
5	164.1	158.7	13	166.9	159.4
6	159.6	128.0	15	158.7	145.4
7	150.0	145.9	16	150.1	138.6
8	153.6	140.4			

Chapter XL.

Clay Products.

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The technology of the clay products offers a peculiarly complex field, dealing as it does with the manipulation of raw materials, which, owing to the low permissible cost factor, must be used largely as nature supplies them, and with processes which are guided by the empirical experience of generations. This involved situation, combined with the complex structure and the unlimited variation of the clays and other silicates, has rendered the scientific attack of the industrial problems very difficult. It is not surprising, therefore, that many of the technical studies, in the endeavor to arrive at useful results as quickly as possible, have been largely empirical. It is only within the last few years that some headway has been made in reducing the variables involved to a reasonable number and in studying fairly well defined systems under controlled conditions. The application of the petrographic microscope and of the X-ray spectrum has been of considerable assistance in the study of the silicates of alumina, in both the hydrous and the anhydrous state. In dealing with the clays some aid has been received from the results of colloid chemistry but for tangible results we are still compelled to resort to our own devices. The more accurate fixation of the physical characteristics, especially of the thermal expansion and the mechanical properties, of our constituent materials has probably assisted as much as anything in extending our knowledge of ceramics.

Clays in the Hydrous State. The properties of clay suspensions are affected by the pH value of the dispersing liquid. Measurements of this constant have been made by Randolph and Donnenwirth[1] but a really satisfactory correlation between the hydrogen ion concentration and such properties as the fluidity of the suspension is still lacking. In practical work the density of the suspension and its fluidity are up to the present time the best criteria for works control.

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[1] *J. Am. Ceram. Soc.*, 9, 541 (1926).

Determinations of the particle sizes of clays by means of the ultramicroscopic motion picture have been made by France [2] at Ohio State University.

In the filterpressing of clay bodies the use of the triple and the diaphragm pumps is on the increase. The application of continuous filterpressing has made a good start. Spurrier [3] considers the presence of included air in plastic clay to be detrimental to its working quality and proposes to subject the material to evacuation followed by a sudden breaking of the vacuum. Galpin [4] has measured the volume of air occluded in clay and finds it to be from 10 to 55% of the original clay volume.

Progress is being made in exhausting the included air from clay suspensions, a procedure which is said to be of considerable benefit. Lapp [5] reports the installation of a vacuum treatment for this purpose. Equipment for the exhaustion of air from clay in the plastic state and attached to the pugging machine has been worked out.

The definition and measurement of the plasticity of clays, as proposed by Bingham,[6] are being given increased attention. In this connection it might be said that the plastometer designed by Green and Haslam [7] could be adapted to the study of the plastic flow of fine grained clays. At the present time the Bureau of Standards is making a study of the work required to force clays through large orifices at different speeds.

For some time the design of more quickly operating apparatus for the determination of the volumes of clay specimens, required in the measurement of drying and firing shrinkages, has occupied several workers. Westman [8] has discussed several types of apparatus for this purpose and has suggested the use of a mercury balance. MacGee [9] has offered a discussion of various types of gas expansion porosimeters for the same kind of measurement.

Clays in the Anhydrous State. While a number of European workers have dealt with the reactions taking place in clays at lower temperatures, during the dehydration period, and at about 1000°, American investigators have concentrated upon the structural changes taking place at the higher temperatures. Navias[10] has used the X-ray method to determine the amount of mullite, $3 Al_2O_3.2 SiO_2$, formed in fired clays and clay-feldspar mixtures, reporting from 33-50% mullite for the ball clays and 50 for the kaolins. A very complete study of the differences between sillimanite, $Al_2O_3.SiO_2$, and mullite as indicated by the Laue and the powder X-ray spectographs has been made by Wyckoff, Greig and Bowen, of the Geophysical Laboratory,[11] who brought out the fact that there are slight but probably real differences between these two crystalline silicates. Previous work by Norton[12] on the X-ray spectra of mullite and sillimanite yielded the same result, and Navias and Davey[13] noted a slight dissimilarity. Some European investigators[14] have not yet fully accepted mullite as the definite decomposition product of clay substance but the fact remains that the evidence obtained so far is in favor of the American results.

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[2] *J. Am. Ceram. Soc.*, **9**, 67 (1926).
[3] *J. Am. Ceram. Soc.*, **9**, 535 (1926).
[4] *J. Am. Ceram. Soc.*, **9**, 587 (1926).
[5] Reported at Detroit meeting of American Ceramic Society, 1927.
[6] *J. Phys. Chem.*, **29**, 1201 (1925).
[7] *Ind. Eng. Chem.*, **17**, 726 (1925).
[8] *J. Am. Ceram. Soc.*, **9**, 311 (1926).
[9] *J. Am. Ceram. Soc.*, **9**, 814 (1926).

It is of interest to note that recent work by Hirsch[15] on the function of silica in ceramic bodies when introduced as crystalline quartz, ground sand and true flint confirms the findings of the Bureau of Standards that quartz promotes translucency while true flint yields bodies of higher mechanical strength. The work of Hirsch, however, is the most complete contribution on the subject.

An interesting study has been made of the microstructure of earthenware bodies by Insley[16] who proved the existence of mullite in low fire bodies of this type.

Specific Heat of Clays. Determinations of the specific heat of clays have been made by MacGee[17] and the heat absorbed computed from the interval values for different temperatures. The clays in undergoing an endothermic reaction at 575° absorb from 60 to 130 calories per gram of dried substance, while at 960° there is an evolution of heat amounting to 25 calories per gram. About 510 calories are required to heat a fire brick body from 25 to 1200°, the specific heat over this interval being 0.43. Ground quartz and feldspar absorb 290 calories per gram in being heated from 0 to 1050°, their specific heats being approximately 0.28. The method employed by MacGee has been criticized by Cohn.[18] Earlier results on the heat absorption of clays obtained by Navias [19] are perhaps still the most accurate that we have.

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[10] *J. Am. Ceram. Soc.*, **8**, 296 (1925).
[11] *Am. J. Sci.*, **11**, 459 (1926).
[12] *J. Am. Ceram. Soc.*, **8**, 401 (1925).
[13] *J. Am. Ceram. Soc.*, **8**, 640 (1925).
[14] *Keram. Rundschau*, **34**, 599 (1926).
[15] *Trans. Ger. Ceram. Soc.*, **7**, 49 (1926).
[16] *J. Am. Ceram. Soc.*, **10**, 317 (1927).
[17] *J. Am. Ceram. Soc.*, **9**, 206 (1926).

Thermal Conductivity. The thermal conductivity of refractories was determined by Norton [20] by means of a new type of apparatus. Taking the conductivities obtained between his extreme temperatures, 200-1400°, values were found from 0.0024 to 0.0042 for fire brick, 0.0047 to 0.0070 for kaolin, 0.0028 to 0.0054 for silica brick, 0.040 for SiC, and 0.0062 to 0.0105 for fused alumina.

Thermal Expansion. A series of measurements of the thermal expansion of refractories was made by Norton.[21] A valuable contribution to the subject was made by Shearer and Wyckoff,[22] who determined the thermal expansion of clays, bodies and glazes and showed clearly the necessity of taking into account this important function in fitting glazes to ceramic mixtures. These workers used the interferometer designed for this purpose at the Bureau of Standards and described by Merritt.[23] The same instrument was employed by Merritt and Peters [24] in measuring the thermal expansion of earthenware bodies and glazes. The interferometer permits of the use of flakes of glaze lifted from the fired ware and thus makes it possible to make measurements upon the glaze as it actually is. The accurate temperature control likewise is of great value.

Electrical Resistivity. This was the subject of an investigation by King.[25] He described a suitable method and conducted his measurements between 713-990°. His findings include the statement that MgO spinel, talc and periclase showed the highest resistance. In this connection it might be proper to call attention to the suggestion of Tammann [26] that in the study of the reactions between solids at elevated temperatures the electrical resistance be used as the means for establishing the presence of a liquidus.

Measurement of Heat Effect. The pyrometric cones used so generally in the ceramic industries for the estimation of time-temperature effects have been subjected to a critical study by Fairchild and Peters[27] of the Bureau of Standards which has demonstrated the reliability of these pyroscopes.

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[18] *J. Am. Ceram. Soc.*, **10**, 347 (1927).
[19] *J. Am. Ceram. Soc.*, **6**, 1268 (1923).
[20] *J. Am. Ceram. Soc.*, **10**, 30 (1927).
[21] *J. Am. Ceram. Soc.*, **8**, 799 (1925).
[22] *The Ceramist*, **7**, 349 (1926).
[23] Bureau of Standards, Scientific Paper No. 485 (1924).
[24] *J. Am. Ceram. Soc.*, **9**, 327 (1926).
[25] *J. Am. Ceram. Soc.*, **9**, 343 (1926).
[26] *Sprechsaal*, **59**, 462 (1926).

Research Activity. There has been a general realization of the importance of fundamental as against empirical research and the Bureau of Standards, the University of Illinois, Ohio State University, Rutgers College, the Massachusetts Institute of Technology, and others have under way studies which deal with the chemical and physical properties of the basic materials and products. A bibliography of the literature on refractories has been published by the American Ceramic Society. It might be of interest to note that in Germany a division for the scientific study of the silicates has been established in the Kaiser Wilhelm Institute.

Industrial Activities. Steady progress is being made in the development of continuous filtering systems, the removal of occluded air from plastic bodies, the casting or pouring of refractories, the further development of the tunnel kiln, the construction of a commercial, electrically heated, tunnel kiln, and the production of super refractories. In the latter field highly aluminous products are being manufactured through the use of minerals like analusite, cyanite and dumortierite, as well as by means of synthetic mixtures of bauxite, diaspore and clay. The ultimate step in this direction has been taken by the Corning Glass Works where mixtures corresponding to the composition of mullite are fused in the electric furnace and cast into tank blocks.

RESEARCH SUGGESTIONS.

1. The principles governing the flow of plastic bodies through orifices.
2. The effect of occluded air in plastic clays.
3. Precise studies of the deflocculation and coagulation of typical clays.
4. The electrical conductivity of clay suspensions and of clays in the plastic state for different water contents.
5. Study of the time-temperature effect in the heating of typical clays and ceramic bodies.
6. Further microscopic and X-ray spectra studies of the structure of clays and ceramic bodies fired to different temperatures.
7. Phase rule studies of simple silicates, borates and boro-silicates in the fused state.
8. Determination of the electrical conductivity of typical silicates and their mixtures during the stages of vitrification and incipient fusion.
9. Study of the dissolved and occluded gases in fused glazes and enamels.
10. Determination of the thermal expansion of typical clays, feldspars and the different varieties of silica fired to a series of temperatures.

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[27] *J. Am. Ceram. Soc.*, 9, 700 (1926).

11. Determination of the thermal expansion of simple silicates, borates and boro-silicates at temperatures up to their softening point, with special reference to the principal silicates and borates of glazes and enamels.
12. Precise determination of the resistance of typical clays and bodies to the several mechanical stresses.
13. Determination of the surface hardness of fired clays, glazes and enamels.
14. Determination of the cause of the rapid thermal expansion of refractory clays between 100° and 200°.
15. Determination of the viscosity of fused glazes and enamels.

Chapter XLI.

Coal, Coke and Gaseous Fuels.

(July 1, 1925-July 1, 1927)

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In reviewing progress of American chemistry of gas and coal during the last two years, the question naturally arises as to how American progress compares with that of Great Britain, Germany and France. In order to obtain some idea of this question the writer has taken as a criterion the number of papers from each country containing experimental data on the subjects of coal (including lignite and peat), and its products—gas, coke and by-products—given in the Fuels Section of Chemical Abstracts for the calendar year 1926. The results of this study are as follows:

Country	Total number of papers for 1926	Total population of country, millions *	Number of papers per million population
United States	104	117	0.88
Germany	103	62	1.66
Great Britain	85	36	2.36
France	31	39	0.80

* 1926, according to World Almanac for 1927.

If we may accept this criterion on a per capita basis the United Kingdom leads in coal and gas research, with Germany next and America and France considerably in the rear.

A further comparison with regard to the nature of the papers shows that the European countries are in the lead of the United States in fundamental research on the constitution of coal and in the processing of coal, such as low-temperature carbonization, liquefaction of coal and the synthesis of chemical products such as methanol, ammonia and hydrocarbons. However, the United States is rapidly forging ahead in applied research in the industrial development of chemical processes based on coal, in the gas and coking industry and in the combustion of coal in central power stations. Some 1700 people attended the International Conference on Bituminous Coal sponsored by the Carnegie Institute of Technology at Pittsburgh, Pa., in November, 1926. Forty-four papers [1] were presented covering the newer developments in coal technology, including the conversion of coal into oil, the synthesis of alcohols and hydrocarbons from water gas, the low-temperature carbonization of coal, the use of pulverized coal and the utilization of by-products of coal carbonization. The success of this conference and the interest in fuel symposia held at the annual meetings of scientific and technical societies indicate a trend toward more research in the fields of coal and gas. It is hoped that this trend will materialize in adequate financial support of the fundamental scientific work, on which industrial developments can be built.

The Constitution of Coal. The basic importance of research on the chemical constitution of coal is self-evident. Parr,[2] in his Chandler lecture, stated that more than 500 separate articles had been published on this subject. The classic monograph which brings together all the information on the subject was first written by Stopes and Wheeler [3] in 1918 and re-published with additional material in 1924.[4]

In February, 1925, at the annual meeting of the American Institute of Mining and Metallurgical Engineers in New York, a symposium was held on coal and coke at which a series of papers on the origin and constitution of coal from the viewpoints of the geologist, the botanist, the microscopist and the chemist were presented [5] by American and British workers in this field of research. Particular attention is drawn to this symposium because it led to international cooperation in the interchange of investigators between the Safety in Mines Research Board and the U. S.

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[1] Proceedings of the International Conference on Bituminous Coal—New Developments in Utilization. Pittsburgh, Carnegie Institute of Technology, 1926. 830 p.

[2] Parr, *Ind. Eng. Chem.*, **18**, 640 (1926).

[3] Stopes and Wheeler, The Constitution of Coal. London, Department of Industrial and Scientific Research, 1918.

[4] Stopes and Wheeler, Fuel in Science and Practice **3** nos. 1-12 (1924).

[5] Thiessen, *Trans. Am. Inst. Mining Met. Eng.*, **71**, 35 (1925); Jeffrey, *Ibid.*, **71**, 149 (1925); Seyler, *Ibid.*, **71**, 117 (1925); Tideswell and Wheeler, *Ibid.*, **71**, 176 (1925); Parr and Hobart, *Ibid.*, **71**, 216 (1925); Fieldner and Davis, *Ibid.*, **71**, 227 (1925).

Bureau of Mines whereby certain differences in nomenclature of the banded constituents of bituminous coal and conclusions regarding the structure of these bands were elucidated.

The alternating bright and dull bands in many bituminous coals have, for years, occupied the attention of investigators of the constitution of coal. Stopes [6] in 1919 proposed the following names for these bands: "Fusain," for the powdery charcoal-like layers called "mother-of-coal" or "mineral charcoal" by other writers; "durain," for the dull band; "vitrain," for the brilliant vitreous band; and "clarain," for the bands of ordinary brightness. According to Stopes the vitrain was a hardened structureless jelly which, when viewed in thin sections by transmitted light under the microscope, showed no plant structures or cell outlines. The clarain showed some plant structures, and durain showed a considerable portion of resistant parts of plants such as spore exines and cuticular material.

Thiessen,[7] however, was unable to confirm the structureless nature of the vitreous bands. He always found typical plant-cell structure in all bright coal bands of American coals. It was therefore a question whether British coals differed from American, or whether a difference of technique in preparing the specimens for microscopic examination was responsible.

On the basis of microscopic examination Thiessen [7] classifies the ingredients of coal as "anthraxylon" and "attritus." Anthraxylon is the undisintegrated coalified wood which shows typical woody cell structure. The bright coal bands are essentially anthraxylon, being the coalified trunks, branches and twigs of trees which were buried in the peat debris. Attritus consists of plant debris which, under the microscope, shows spore and pollen exines, cuticles, bits of resistant plant tissues intermixed with resinous, carbonaceous and mineral matter. The dull bands of coal are made up of strips of anthraxylon in a ground mass of attritus.

In the summer of 1926, Thiessen was detailed by the Bureau of Mines to Wheeler's laboratory at Sheffield University, England, for a year to work with some of the British investigators on the constitution of coal with the object of reconciling the apparent differences in structure of British and American coals, or possibly the differences in microscopical technique. The results of this mission constitute one of the most important contributions of the past year to our knowledge of the constitution of coal. Thiessen was able to show plant-cell structure in all of the British vitrains he examined, although he found it extremely difficult to prepare sections thin enough to bring out this structure by transmitted light, because of the more highly carbonized condition of British coals as compared to American bituminous coal. Hence, the British vitrain is not a hardened structureless jelly as originally supposed, although the plant structure is less recognizable than in most American bituminous coals.[8]

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[6] Stopes, *Proc. Roy. Soc.*, **90B**, 470 (1919).
[7] Thiessen, Bur. Mines, Bull. no. 117 (1920).

Morgan,[9] in a summary of recent progress in the study of the constitution of coal, has classified the chief methods which have been used to furnish information on the constitution of coal as follows:

1. Microscopical examination.
2. The use of solvents which aim to separate, in a condition not much altered, some of the components of the coal.
3. The use of reagents and a study of the reaction products.
4. A study of the products of destructive distillation.
5. The synthesis of artificial coals including synthesis of "ulmic substances."

Microscopical Examination. The outstanding work of Thiessen of the Bureau of Mines has been described.

Jeffrey[5] considers coal—outside of ash content—to consist of three main materials, more or less modified by water action, heat and pressure—namely, (1) spores; (2) a dark matrix, structureless and difficultly penetrated by light; and (3) wood. The spores are sources on destructive distillation of hydrocarbons—liquid and gaseous. Spores predominate in cannel coals and oil shales. Spore coals do not coke. The woody constituent is the glossy bright band in bituminous coal, and anthracites. This glossy bright constituent which Thiessen terms "anthraxylon" imparts the coking properties to a coal, provided the wood has been modified to the proper degree in the coalification process to fuse on heating. These deductions agree with Thiessen's except that Thiessen finds more structure in the dark matrix when it is subjected to special microscopical examination.

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[8] Thiessen, *J. Roy. Soc. Arts,* **74,** 535 (1926).

[9] Morgan, *in* Monograph on Recent Progress in Science in Relation to the Gas Industry. New York, Am. Gas Assoc., 1926.

St. John[10] has reviewed the work of Kemp and McLaren in applying X-rays to the determination of inorganic matter and pyrite in coal in connection with coal-washing processes and discusses the possibilities of the study of coal by direct radiographs, Laue photographs, and X-ray spectographs.

Turner,[11] by heat-etching polished sections of anthracite, has shown that plant structure similar to that shown by Thiessen in the examination of thin sections of bituminous coal exists in anthracite. The evidence is now complete that the primary raw material is vegetable matter, in all ranks of coal from the German brown coal and the American lignites, through the various types of bituminous coal to the highest rank of anthracite.

Action of Solvents and Reagents on Coal. The extraction of coal with organic solvents has long been a favorite method of attack for separating the constituents of coal into groups in the least changed, if not entirely unchanged condition. Pyridine, benzene, phenol, chloroform, ether, etc., are the principal solvents that have been used. Pyridine, phenol, benzene and xylene—the latter two under pressure—are among the most effective solvents, although it is a question whether the increased action of benzene and of xylene under pressure at temperatures of 270-280° C. is not due to a partial decomposition of the coal. For this reason Wheeler[12] and the British coal chemists prefer to use pyridine and chloroform for separating coal constituents into three groups termed alpha, beta, and gamma compounds. The amount of material extracted by boiling pyridine varies from almost zero, with anthracite, to 35 and 40% in good gas coals.

Fischer[13] obtained an analogous separation of coal into these groups of constituents, by heating with benzene at 275° C. under 55 atmospheres pressure. The residue was non-coking, similar to the alpha and beta products of the pyridine-chloroform treatment. The extract contained the constituents responsible for the coking and swelling properties of coal, when the coal is subjected to destructive distillation. These soluble constituents, which they called "bitumens," were separated by further treatment with petroleum ether, into a soluble oil which, according to their experiments, was the cementing agent of the coke, and an insoluble, hard, waxy residue which seemed responsible for the swelling of the coking mass. However, Davis and Reynolds[14] of the Bureau of Mines, found that the application of Fischer's benzene extraction to a Utah non-coking coal and a Pittsburgh coking coal yielded a solid "bitumen" which had more coking power than the oily "bitumen," a result somewhat at variance with those of Fischer.

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[10] St. John, *Trans. Am. Inst. Mining Met. Eng.*, **74**, 640 (1926).
[11] Turner, *Trans. Am. Inst. Mining Met. Eng.*, 71, 127 (1925).
[12] Wheeler and Burgess, *J. Chem. Soc.*, **99**, 649 (1911).
[13] Fischer, *Ind. Eng. Chem.*, **17**, 707 (1925).

By extracting Illinois coking coal in both the fresh and oxidized state with xylene under pressure at temperatures of about 250° C., Parr[2] has shown that the residues of both the fresh and oxidized coal did not coke on heating, although before extraction the fresh coal coked and the oxidized coal did not. He also found that the mixture of the residue from the fresh coal with the extract from the fresh coal coked like the original coal, whereas the residue from the oxidized coal mixed with the extract from the fresh coal did not coke. Therefore, it appears that the coking property of the coal is in the xylene extract but this property may be destroyed by the oxygen of the oxidized xylene residue. Parr's[5] experiments also showed that the xylene-insoluble residue, which probably contains most of the "humic" or "ulmic" constituents of coal, oxidizes much more rapidly and to a much greater extent than the extract. However, this conclusion varies somewhat from some experiments by Davis and Reynolds,[15] in which a non-coking Utah coal was extracted with benzene under pressure and the extract separated with petroleum ether into oily and solid "bitumens," according to the method of Fischer. They found that when the oily and solid bitumens were dispersed on pumice, so as to give a large surface exposure, and then oxidized with air for 100 hours at 60° C., the two extracts absorbed oxygen and gave off carbon dioxide and water vapor at about the same rate as the residue from the xylene extraction. Each of the three fractions oxidized more rapidly than the raw coal. They attribute the greater rate of oxidation of the fractions to the greater surface exposed. The xylene residue was presumed to be more porous than the original coal owing to the extractive action of the xylene.

Spontaneous Combustion of Coal. Davis and Byrne[16] of the Bureau of Mines found that pulverized coal which contained from 2 to 10% moisture did not heat in a current of dry oxygen until after the moisture had been removed. Instead, there was an actual cooling of the coal due to evaporating water. However, when the coal was subjected to excessive drying—that is, prolonged heating at 140°C. in a current of thoroughly dried nitrogen or in a high vacuum, then no appreciable spontaneous heating took place on passing oxygen over the thoroughly dried coal, at a temperature of 70°C. Apparently a trace of moisture is needed to promote oxidation.

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[14] Davis and Reynolds, *Ind. Eng. Chem.*, 18, 838 (1926).
[15] Davis and Reynolds, *Fuel in Science and Practice*, 5, 405 (1926).
[16] Davis and Byrne, *Ind. Eng. Chem.*, 18, 233 (1926).

At the University of Illinois, Li and Parr [17] studied the action of marcasite and pyrite in promoting spontaneous combustion of coal. They found that these minerals oxidize at about the same rate, but the former breaks down more easily, producing fine particles, thus facilitating its oxidation. However, the rate of oxidation of similar coals is not proportional to the pyritic content. Moisture was found to be a necessary factor and the admixture of certain clays appeared to act catalytically in promoting oxidation. They conclude that under certain conditions the pyrite may oxidize rapidly at ordinary temperatures and produce local temperatures sufficiently high (75-85°) to initiate readily the oxidation of the carbonaceous substances.

Absorption of Gases by Coal. Like other colloidal substances coal absorbs gases to a considerable extent. Sinkinson and Turner [18] at Lehigh University found that anthracite absorbed more CO_2 (80—200 cc./10 g. coal) and evolved more heat (2—4° temperature rise) than bituminous coals (15—50 cc./10 g. coal and 0—1.5° temperature rise) or samples of fusain from the anthracite beds.

Fusibility of Coal Ash and Clinker Formation. The Bureau of Mines,[19] in cooperation with the American Society for Testing Materials, has completed the standardization of the gas-furnace method for determining the fusibility of coal ash; and in cooperation with the Carnegie Institute of Technology, the New York Edison Company, and the Consolidated Gas Company of New York has conducted research on the relation between the fusibility of coal ash and clinker formation in fuel beds. A first report [20] on this work shows that the average quantity of clinker formation relative to the total ash in the coal and also the size of the clinker pieces seems to have a fairly definite relation to the softening temperature of the coal ash as determined by the standard gas-furnace method. Clinker formation does not take place to any material degree with coals having ash-fusing temperatures above 1450°C. Close agreement of results was obtained in determining fusing temperatures by the Standard American method and the Sinnatt method used in England, but results by the micropyrometer method did not agree with either of the above two methods, nor did the micropyrometer results bear any close relation to the clinkering in the experimental furnace.

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[17] Li and Parr, *Ind. Eng. Chem.*, **18**, 1299 (1926).

[18] Sinkinson and Turner, *Ind. Eng. Chem.*, **18**, 602 (1926).

[19] Fieldner and Selvig, *Fuel in Science and Practice*, **5**, 24 (1926).

[20] Selvig, Nicholls, Gardner and Muntz, Carnegie Inst. Tech., Mining Met. Investigations, Bull. no. 29 (1926).

Analyses of American Coals. Ever since the establishment of the Government Fuel Testing Plant at St. Louis in 1903, the U. S. Geological Survey, and since 1910, the Bureau of Mines, have been making analyses of American coals which have been published from time to time. In recent years these analyses, together with descriptions of the coal beds from which the samples were taken, have been collected and published in separate technical papers, each covering a single State. During 1925 and 1926 the Bureau of Mines issued seven publications.[21]

Methods of Testing and Analyzing Coal and Coke. Committee D-5 on Coal and Coke, of the American Society for Testing Materials, has become the recognized authority on standard American methods. Progress in the last two years has consisted of the following:

1. The adoption of the gas-furnace method developed by the Bureau of Mines, as a standard for determining the fusibility of coal ash.[22]

2. The adoption of a method of test for the fineness of powdered coal, as a tentative standard.[23]

3. The outlining of a tentative method for sieve testing of anthracite.[24]

4. The adoption of the bomb-washing and the peroxide method as standard alternate methods with the present Eschka method for the determination of sulfur in coal and coke.

This was done after 16 samples of coal and coke, ranging in sulfur content from 0.5 to 17% were analyzed for sulfur by 5 different laboratories by the bomb-washing, peroxide, and Eschka methods. The results check equally well by each of the three methods.[25]

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[21] Bur. Mines, *Tech. Papers*, nos. 345, 347, 356, 365, 366; Reports of Investigations no. 2708; Pa. Topographic and Geol. Sur., Bull. M 6, pt. IV.

[22] Committee D-5, *Proc. Am. Soc. Testing Materials*, **26**, 412 (1926).

[23] *Proc. Am. Soc. Testing Materials*, **26**, 417, 898 (1926).

[24] *Proc. Am. Soc. Testing Materials*, **26**, 421 (1926).

[25] Selvig and Fieldner, *Ind. Eng. Chem.*, **19**, 729 (1927).

Cooper and Osgood [26] of the Bureau of Mines investigated the influence of crucible materials on the results of volatile-matter determination by the A. S. T. M. standard electric-furnace method. They found that the results obtained with illium alloy and vitreosil crucibles checked those obtained with platinum within the limits set by the American Society for Testing Materials (0.5% for anthracite and bituminous coal, and 1.0% for lignite) in most cases, the exceptions being in a few high-volatile, non-coking coals, and lignites. However, platinum permitted faster work on account of its lower heat capacity and greater durability.

Combustion of Coal Dust. Research on the mechanism of ignition and propagation of flame in coal-dust suspensions in air is important in connection with the limitation and prevention of dust explosions in coal mines and industrial plants; and in connection with firing pulverized coal in boilers and other furnaces. Research with a view to explosion prevention is an important part of the research program of the U. S. Bureau of Mines. Cooperative experiments [27] with the Safety in Mines Research Board of Great Britain conducted on British and American coals in both England and America have resulted in a standardization of coals and methods which makes it possible to coordinate research programs and to make the results mutually available. A second step in this international cooperative research was the study of the effect of release of pressure on the development of coal-dust explosions, by Greenwald [28] of the U. S. Bureau of Mines and Wheeler of the British Safety in Mines Research Board. Experiments in a gallery 7½ feet in diameter and 750 feet long at Sheffield, England, led to these conclusions, other conditions remaining constant:

1. The prevention of release of pressure behind the point of ignition is more favorable to the inception of a coal-dust explosion than is partial or complete release.

2. The influence of openings along the path of an explosion is mainly one of release of pressure; so that when the openings are ahead of the flame its velocity is increased, and when they are behind the flame its velocity is decreased.

In view of the high cost of large gallery and experimental mine tests of the relative explosibility of various coal dusts, both American and foreign investigators have sought to develop laboratory-scale testing galleries. Allison[29] of the Bureau of Mines has described a steel gallery 8 inches in diameter and 17 feet long and has determined the relative explosibility of a number of coal and other combustible dusts in this gallery. However, the results obtained are approximate only and cannot be taken as representative of large-scale tests. Little is known of the influence of particle size on rate of combustion of coal-dust particles. Bouton and Pratt[30] of the Bureau of Mines developed an air-elutriation method by which fine coal dust, all through 200-mesh sieve, could be separated into four size-groups of particles, namely, 0-10, 10-15, 15-25, 25-74 microns. Bouton and Hayner[31] determined the relative flammabilities of these four groups and found that the very finest particles developed less pressure on flammation in a closed flask than did the groups between 10 to 25 microns, which gave the maximum pressures.

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[26] Cooper and Osgood, *Fuel in Science and Practice*, 5, 381 (1926).

[27] Rice and Wheeler, Safety in Mines Research Board, Paper no. 13 (1925).

[28] Greenwald and Wheeler, Safety in Mines Research Board, Paper no. 14 (1925).

With reference to the combustion of pulverized coal, Kreisinger[32] has pointed out that the length of visible flames depends upon the volatile matter in the coal, its composition, the amount of primary air, and the method of mixing coal and air. The velocity of combustion mainly depends upon the rate and manner of mixing of the gases and the fuel during combustion. Recent developments in burning powdered coal under steam boilers were discussed by Kreisinger[33] at the International Coal Conference of Carnegie Institute of Technology last November.

Coke. Powell[34] and Rose[35] of the Koppers Company Laboratories have written two excellent summaries, the former on "Physical and Chemical Properties of Coke in Relation to its Manufacture and Use" and the latter on "The Selection of Coals for the Manufacture of Coke."

Rose[36] also has developed a method of polishing and treating coke surfaces whereby the cell structure is shown with remarkable sharpness and in perfect form for photographic reproduction. After preliminary rough grinding to a flat section, the surface is coated with a mixture of 98% plaster of Paris and 2% magnesium oxide. The surface is then ground down with silicon-carbide powder of increasing fineness, renewing the plaster coating as necessary, and finally polishing with levigated alumina.

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[29] Allison, *Trans. Am. Inst. Mining Met. Eng.*, **74**, 392 (1926).

[30] Bouton and Pratt, Carnegie Inst. Tech., Mining Met. Investigations, Bull. no. 12 (1924).

[31] Bouton and Hayner, Carnegie Inst. Tech., Mining Met. Investigations, Bull. no. 22 (1925).

[32] Kreisinger, *Ind. Eng. Chem.*, **17**, 1232 (1925).

[33] Kreisinger, International Conference on Bituminous Coal, p. 361 (1926).

[34] Powell, Recent Progress in Science in Relation to the Gas Industry, p. 8 (1926)

[35] Rose, Recent Progress in Science in Relation to the Gas Industry, p. 21 (1926); *Trans. Am. Inst. Mining Met. Eng.*, **74**, 600 (1926).

[36] Rose, *Ind. Eng. Chem.*, **17**, 895 (1925).

During the past two years the Bureau of Mines has continued research on the combustibility and reactivity of coke. Sherman and Kinney[37] determined the relative combustibility of several beehive cokes, by-product cokes, and a wood charcoal, using a wind furnace of one square foot grate area, a 12-inch deep fuel bed, fuel sized between 1 and 1.5 inches, and a rate of combustion of 20 to 25 pounds per square foot of grate area. Gases were collected from different levels in the fuel bed and analyzed for CO_2, CO, and O_2. The mean combustibility was calculated from the following equation:

$$\text{Mean combustibility} = \frac{100\,(CO_2 + CO)}{2(CO_2 + O_2) + CO}$$

Three beehive cokes gave 69, 73, and 72% combustibility; an oven-wall by-product coke 67%; an underheated by-product coke 77%; and a wood charcoal 95%. These results together with those obtained earlier by Sherman and Blizard[38] show that the principal factor which influences rate of combustion is the size of the coke pieces, in the case of ordinary high-temperature by-product and beehive coke, although selected ends from next the oven-wall are less combustible, and strongly under-coked material seems more combustible than the average. No relation was found between porosity and combustibility.

Recently, in connection with a study of cokes from various types of plants using the same coals,[39] made in cooperation with the Carbonization Committee of the American Gas Association, Nicholls, Brewer, and Taylor of the Bureau of Mines have further improved and standardized the wind-furnace method of determining combustibility, so that more closely agreeing results can be obtained than formerly. However, the numerical values now obtained for combustibility are not directly comparable to the figures of Sherman. The order of relative reactivity is essentially the same in the wind furnace and the laboratory-tube furnace, a surprisingly good agreement when we consider the difference in conditions of test. Likewise the most reactive and least reactive cokes in air maintain the same position in water vapor and carbon dioxide. Therefore distinct progress has been made in research in coke reactivity but much more remains to be done in determining the factors which control reactivity.

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[37] Sherman and Kinney, *Fuel in Science and Practice*, 5, 98 (1926); Sherman, *Iron Age*, **115**, 1043 (1925).

[38] Sherman and Blizard, *Trans. Am. Inst. Mining Met. Eng.*, 69, 526, 584 (1923).

[39] Nicholls, Brewer and Taylor, *Proc. Am. Gas Assoc.*, Carbonization Com. Rept., **1926, 1129.**

Haslam and Ward[40] at Massachusetts Institute of Technology also studied the same five cokes from the American Gas Association plant tests and determined the relative ease of ignition, air required to sustain combustion during banking, and suitability for water-gas reactions. These results, together with physical and chemical tests made by the Bureau of Mines, constitute the first comparison of cokes from various types of gas plants using the same coal. The only outstanding difference in the cokes from the various plants was in the apparent density; the cokes from the horizontal retort plant and the continuous vertical were much lighter than those from the intermittent vertical retorts and intermittent oven-type plants.

Producer Gas and Water Gas. *Gas-Producer Reactions.* The Department of Gas and Fuel Engineering of Massachusetts Institute of Technology has continued research on gas-producer reactions. Haslam, Mackie, and Reed[41] from experiments on a small producer, with anthracite fuel beds varying in depth from 1.5 to 4.5 feet; firing rates from 10 to 70 pounds of coal per square foot of grate area per hour; and a constant steam rate of 0.4 pound per pound of coal, concluded (1) that the cold gas efficiency, the heating value of the gas, and the percentage of steam decomposed are all increased by increasing either the firing rate or the depth of bed; (2) that the thickness of the oxidation zone and of the primary reduction zone are independent of the firing rate or the total depth of fuel; (3) that the improved results obtained by increasing the firing rate, or the depth of bed are due to the increased temperature of the primary reduction zone.

In another series of experiments at a firing rate of 40 pounds of coal per square foot grate area per hour, Haslam, Ward, and Mackie[42] found the optimum steam ratio to be 0.7-0.8 pound of steam per pound of coal. This optimum value increased with increased rate of firing. The thickness of the oxidation and of the primary reduction zones were independent of the steam ratio, but the temperature of the primary reduction zone decreased with an increasing ratio.

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[40] Haslam and Ward, *Proc. Am. Gas Assoc., Carbonization Com. Rept.*, 1926, 1120.

[41] Haslam, Mackie and Reed, *Ind. Eng. Chem.*, 19, 119 (1927).

[42] Haslam, Ward and Mackie, *Ind. Eng. Chem.*, 19, 141 (1927).

Goff,[43] applying the laws of chemical equilibrium to the reactions in a gas producer, has made an analysis of the possible reactions and has deduced the distribution of total carbon between the three principal reactions—namely, $C + O_2 = CO_2$; $C + 2H_2O = CO_2 + 2H_2$; and $C + CO_2 = 2CO$ for the temperature range 1300-2400° F. From his theoretical analysis he concludes the efficiency is a maximum (84%) at 2000° F. above which temperature it drops off slightly; 0.4 pound of water per pound of carbon is the water consumption for this maximum efficiency. The percentage composition of the wet gas corresponding to the temperature of maximum efficiency is 34.7 CO, 1.7 CO_2, 10.6 H_2, 0.5 H_2O, and 52.4 N_2.

Production of Water Gas. The growing use of bituminous coal instead of coke, and experimentation on the use of oxygen are the principal events of the last two years in the technology of water-gas production. Fulweiler has summarized recent progress in water-gas manufacture [44] and also has reviewed the utilization of bituminous coal [45] in the manufacture of water gas.

Dunkley [46] and others of the Bureau of Mines conducted tests on large water-gas sets which showed that the bituminous coals of the Middle West could be used successfully, and later the work of Murdock and others [47] resulted in the development of the Pier Process which increased capacity and reduced fuel consumption. Further experimentation showed the great importance of the softening characteristics of the coal used, uniformity of size,[48] and freedom from fines.

Use of Oxygen for Gas Making. According to McBride,[49] who has recently reviewed the use of oxygen for gas-making, serious attention to this subject was first suggested in 1920 by F. G. Cottrell, then Director of the U. S. Bureau of Mines. A few trials in the use of oxygen for making oil gas by the Dayton process, conducted at Irvington, N. J., showed 71 to 80% thermal efficiency, yielding a gas of 543 B.t.u. per cubic foot.[50] At

[43] Goff, *Ind. Eng. Chem.*, 18, 585 (1926).

[44] Fulweiler, Recent Progress in Science in Relation to the Gas Industry, p. 30 (1926).

[45] Fulweiler, International Conference on Bituminous Coal, p. 472 (1926).

[46] Dunkley, Bur. Mines, Tech. Paper no. 335 (1925).

[47] Murdock, *Proc. Am. Gas Assoc.*, 1924, 766; Novak, *Ibid.*, 1925, 1194; Rudd, *Am. Gas J.*, 123, 444 (1925); Parker, *Am. Gas J.*, 123, 217 (1925).

[48] Gilliland, *Gas Age-Record*, 55, 641 (1925).

[49] McBride, Recent Progress in Science in Relation to the Gas Industry (1926).

[50] Frey, *Proc. Am. Gas Assoc.*, 1925, 1223.

first thought it would appear that a continuous gasification process of high-thermal efficiency could be developed, by using oxygen with sufficient steam to control the fuel-bed temperature. Unfortunately the reaction velocity of the combustion of carbon to carbon dioxide is much greater than the reduction of carbon dioxide or water vapor by carbon. Haslam, Entwistle, and Gladding[51] demonstrated that most of the oxygen present would react with the coke to form CO_2 before any material reaction between the steam and coke could begin. Hence, the endothermic reaction with steam would not be available for reducing the temperature in the narrow oxidizing zone.

Parr and Vandaveer's[52] experiments with a small generator (5 in. by 10 in. by 5 ft.) at the University of Illinois also indicated that the oxidation-zone temperature would be sufficiently high to slag the ash. The gas obtained was of rather low heating value due to the high CO_2 content.

On the other hand, White and Chamberlin[53] at the University of Michigan, from laboratory experiments using an electrically heated tube 2.5 inches in diameter by 36 inches high, and held at a temperature of 1800 to 2000° F., concluded that the temperature was readily controllable by steam during gasification. However, this is done at the cost of a high CO_2 content (23%) in the gas made. Large scale experimentation is needed before definite conclusions on the practicability of operation with oxygen can be made. If oxygen could be produced very cheaply, means no doubt could be developed to operate the apparatus as a slagging gas producer.

High-Temperature Carbonization of Coal. The principal advance in high-temperature carbonization in recent years is in improved coke-oven design which increases the output. These ovens are usually narrower and admit of the use of higher coking temperatures, thus shortening the time of carbonization and permitting the use of coal of higher oxygen content. Similar improvements have been made in retorts and ovens for gas making purposes.

Beebee[54] has reported experiments at Rochester, N. Y., with the new Sultzer dry-quenching process. Results have more than met expectations in heat recovery and elimination of the clouds of steam which are objectionable on account of the location of the plant in the business district of the city.

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[51] Haslam, Entwistle and Gladding, *Ind. Eng. Chem.*, 17, 586 (1925).
[52] Vandaveer and Parr, *Ind. Eng. Chem.* 17, 1123 (1925).
[53] White and Chamberlin, *Am. Gas Assoc. Mo.*, 7, 757 (1925).
[54] Beebee, *Gas Age-Record*, 59, 413 (1927).

On the scientific side of carbonization research, Davis, Place and Edeburn[55] of the Bureau of Mines have determined the sum of exothermic and endothermic reactions obtained by carbonizing small samples of coal in the absence of air at temperatures up to 650°C. in twin adiabatic calorimeters. The total heat effect was usually exothermic, but very small with typical coking coals. As the oxygen content of the coal increased the exothermic heat increased to a maximum of about 50 calories per gram.

Burke and Parry[56] of the Combustion Utilities Research Laboratories have corroborated these values, using a different method involving the heating of approximately 17 pounds of coal by the sensible heat of inert flue gases of constant composition, in a light sheet-metal retort. Heat losses were eliminated within limits of experimental error, by surrounding the retort with an electrically heated chamber, whose temperature could be kept equal to the retort. The heat input and output of the heating gases were measured and from these, the heat absorbed or given off by the carbonizing coal was calculated. The following exothermic values were obtained:

Coal	*B.t.u. per lb.*
Denver sub-bituminous	85
Utah non-coking	37-59
Pittsburgh	7

The rate of travel of the fusion zone in by-product coke ovens was measured by Ryan[57] of the Massachusetts Institute of Technology. He found that the curves for the rate of travel of the fusion zone, or of isotherms below 1100°F. through the charge are in agreement with those calculated from the rate of heating of a solid slab of constant heat capacity and conductivity, which is heated by walls of constant temperature. This indicates that the thermal characteristics of the coal, plastic coal and semi-coke, are all of the same order of magnitude and the heat effects of fusion and thermal decomposition are negligible. As the charge is heated above 1100°F., however, its heat conductivity increases suddenly to several times its original value.

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[55] Davis, Place and Edeburn, *Fuel in Science and Practice*, **4**, 286 (1925).
[56] Burke and Parry, *Ind. Eng. Chem.*, **19**, 15 (1927).
[57] Ryan, *Proc. Am. Gas Assoc.*, **1925**, 861; *Fuel in Science and Practice*, **5**, 150 (1926).

Since the rate of travel of the fusion zone decreases as the distance from the heating wall increases, until the effect of preheating at the center of the oven causes the rate of travel to increase again as it nears the center, it is evident that the greater the oven width the lower will be the minimum rate of travel reached before the increase takes place. Hence, since the initial and the final (at wall and at center) rate of travel are the same, regardless of the oven width, it is seen that the wider the oven the lower the average rate of travel of the fusion zone. This explains the greater output per volume unit of the newer types of narrow coking ovens.

The carbon bisulfide found in coal gas has usually been considered a secondary reaction product of hydrogen sulfide and hot coke. Huff [58] has given some experimental evidence that it is a primary product of coal carbonization, because on rapid heating of small quantities of coal appreciable amounts of CS_2 were found, but on slow heating and free gasification only hydrogen sulfide was found.

BY-PRODUCTS OF HIGH-TEMPERATURE CARBONIZATION.—*Tar.* Virtually all American research on tar during the last two years has been in the field of low-temperature carbonization, to which reference will be made under the heading of by-products of low-temperature carbonization. There has been one contribution applicable to both high-temperature and low-temperature tars—namely, that of Morgan and Meighan [59] of Columbia University, on the extraction of phenols from tar oil by the caustic soda process. From a series of experiments these investigators found that the optimum NaOH concentration for maximum phenol extraction was 23.5% for Doherty hydrogas tar including distillate up to 365°C., and was 19.0% for coke-oven tar oil. They conclude that the best concentration and conditions must be worked out experimentally for each kind of tar.

Technologists interested in coal tar will find a comprehensive review of progress, during the last two decades, in Chapter VIII of "Recent Progress in Science in Relation to the Gas Industry," entitled "Tar Refining and Tar Products," by Weiss. Also at the Coal Conference at Pittsburgh in November, 1926, Church presented a paper on "The Utilization of Tar Products," and Weiss a paper on "Coal Tar Disposal" (disposal referring to sale or working-up of the tar into commercial products).

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[58] Huff, *Ind. Eng. Chem.,* 18, 357 (1926).

[59] Morgan and Meighan, *Ind. Eng. Chem.,* 17, 696 (1925).

Phenol wastes.—The expansion of the coke and gas industry has brought in its train the problem of disposing of phenol-bearing wastes, without discharging them directly into streams where they may be detrimental to aquatic life or cause the development of an objectionable taste when the phenol-polluted water is subsequently chlorinated for city water supplies. Brown [60] of the Bureau of Mines has reviewed the sources of phenol wastes, and has described various methods proposed and tried for their disposal. One of the most promising methods of recovery is that of Crawford,[61] in which the phenols are extracted from the weak ammonia liquor with benzol, instead of trying to remove them from the ammonia still waste, as in methods previously suggested. The phenols are then extracted from the benzol solution by NaOH solution from which they are liberated by carbon dioxide or sulfuric acid. The process shows a continuous plant efficiency of 95 to 99%. Crawford has described also a modified process using Na_2S solution to extract the phenols from the benzol solution. The sulfide extract is then neutralized with H_2S and, after separating the liberated phenols, the final solution of $Na_2S + NaHS$ is boiled to liberate H_2S and regenerate Na_2S, both returning to the process. The Crawford process is in operation at a coke-oven plant at Troy, New York. Crawford [62] has suggested that it is feasible and profitable to recover phenols from steel plant fuel tars.

Heffner and Tiddy [63] have proposed a process in which the gas liquor high in ammonia content is preheated before entering the ammonia still, and the vapors are allowed to leave the still at a sufficiently high temperature to prevent recondensation of the ammonium phenolate which is formed in the still. The ammonium phenolate is recondensed when cooled below 98°C., after leaving the still.

Low-Temperature Carbonization. Low-temperature carbonization and allied processes, whereby a greater yield of liquid by-products together with a more easily ignitible and more combustible smokeless solid fuel is obtained than in high-temperature carbonization, have received considerable attention in recent years in spite of the fact that a number of attempts to commercialize such processes in the last 15 or 20 years have failed.

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[60] Brown, *Am. Gas Assoc. Mo.*, 8, 211, 240, 254, 279 (1926).
[61] Crawford, *Ind. Eng. Chem.*, 18, 313 (1926); 19, 168 (1927).
[62] Crawford, International Conference on Bituminous Coal, p. 457 (1926).
[63] Heffner and Tiddy, U. S. P. 1,566,795 and 1,566,796 (Dec. 22, 1925).

According to Porter[64] and Fieldner,[65] who have published several general reviews of the subject, the principal processes under commercial or semi-commercial scale experimentation in the last two years are:

1. The Carbo-Coal or McIntire process of the Consolidation Coal Products Co., Fairmont, W. Va.[66] 2. The Piron-Caracristi process at Ford Motor Co., Walkerville, Ontario.[67] 3. The Green-Laucks process of the Old Ben Coal Corporation of Illinois.[68] 4. The McEwen-Runge process of the International Combustion Engineering Corporation at the plant of the Milwaukee Heat, Light and Power Co. at Milwaukee, Wisconsin.[69] 5. The Parr process at the University of Illinois.[2, 70] 6. The Carbocite process.[71] 7. The White "crushed coal" process.[72]

Of these processes, the McIntire plant has operated continuously over the longest period and has demonstrated that a satisfactory smokeless fuel briquet can be made. It may be regarded as technically successful; whether economic conditions and markets permit of profitable operation is another question which is not yet proved.

The Piron-Caracristi plant at the Ford Motor Works has been discontinued. The others are still in the developmental stage.

The McEwen-Runge and the White processes are of special interest because of the rapid heat transfer permitted by crushing the coal to small particles. Both processes shower the crushed coal down a tall retort. In the former process the coal is heated by the sensible heat of preheated inert gases; in the latter the coal is carbonized by radiant heat from the hot retort walls.

Parr's process is of interest because of the application of scientific principles of coal carbonization that he has worked out in relation to the constitution of coal.[73] These are: (1) The avoidance of oxygenation; (2) the lowering, as far as may be possible, of the oxygen content of the coal; (3) the removal of the initial gaseous products of decomposition such as CO_2 and H_2O which occur before the pasty or carbonaceous stage of decomposition has been reached; and (4) the quick approach to the softening temperature.

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[64] Porter, *Proc. Am. Gas Assoc.*, 1926 and 1927; International Conference on Bituminous Coal, p. 599 (1926).

[65] Fieldner, Bur. Mines, Tech. Paper no. 396 (1926); Reports of Prime Movers Committee, Nat. Elec. Light Assoc., 1925-1927.

[66] McIntire and Thomson, *Ind. Eng. Chem.*, 19, 12 (1927); *Power Plant Eng.*, 30, 579 (1926); International Conference on Bituminous Coal, p. 650 (1926).

[67] Caracristi, *J Franklin Inst.*, 202, 323 (1926); Piron and Crawford, International Conference on Bituminous Coal, p. 729 (1926).

[68] Green, International Conference on Bituminous Coal, p. 712 (1926); Laucks, *Ind. Eng. Chem.*, 19, 8 (1927).

[69] Runge, International Conference on Bituminous Coal, p. 697 (1926); *Coal*, 1, 196 (1926).

[70] Parr, International Conference on Bituminous Coal, p. 635 (1926).

[71] Wisner, International Conference on Bituminous Coal, p. 800 (1926).

[72] White, International Conference on Bituminous Coal, p. 419 (1926).

The carbonization of non-coking coals has been discussed by Odell,[74] with particular reference to lignite.

By-Products of Low-Temperature Carbonization. Strictly chemical research on low-temperature carbonization has been directed principally toward an elucidation of the composition of the gases, light oils and tar.

Low-temperature gas and light oils. Frey and Yant,[75] at the Bureau of Mines, after working out a method for the separation of the individual saturated and unsaturated hydrocarbons in coal gas, by fractional distillation at low temperatures, made complete analyses of (1) the gas from the distillation at low temperature, in an atmosphere of superheated steam, of a Utah non-coking coal; (2) low-temperature gas from the McIntire externally heated retort, using Pittsburgh coking coal; and (3) high-temperature gas from a by-product coke oven using Pittsburgh coking coal.

Brown and Cooper,[76] also at the Bureau of Mines, determined the composition of the light oils collected from the same tests on which Frey and Yant examined the gas obtained by carbonizing a non-coking Utah coal by internal heating with superheated steam.

About 1.7 gallons of light oil per ton of coal carbonized were recovered, which distilled between 20 and 200°C.

Low-temperature tar.—According to Weiss,[77] low-temperature tars are not as well known as the older high-temperature tars. They vary quite widely because the conditions of production are not standardized. In general, aromatic hydrocarbons are absent, and the bulk of the distillable material consists of paraffins or saturated cyclic hydrocarbons along with varying amounts of unsaturates. Phenols are always present in large amounts, very little true phenol or cresols being present, the bulk consisting of high-boiling tar acids of which little or nothing is published regarding their chemical constitutions.

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[73] Parr, *Trans. Am. Inst. Mining Met. Eng.*, **74**, 474 (1926).

[74] Odell, *Proc. Am. Gas Assoc.*, 1925, 879.

[75] Frey and Yant, *Ind. Eng. Chem.*, **19**, 21, 488, 492 (1927).

[76] Brown and Cooper, *Ind. Eng. Chem.*, **19**, 26 (1927).

[77] Weiss, Recent Progress in Science in Relation to the Gas Industry, Chapt. VIII (1926).

Less pitch is obtained from the low-temperature tars than the high-temperature tars, and the natures of the residues are quite different. There is a broad field of work in the future for studies involving the nature and best sphere of usefulness of these materials and much work is in progress, both in this country and abroad.

Morgan,[78] in discussing the "Composition and Economic Value of Low-Temperature Tar," states that he believes there are very great possibilities for use of low-temperature phenols as chemical raw material, but the development of these uses will take years of patient research, the rewards of which should belong to those who make the developments. He sees no escape, therefore, from the conclusion that at present or in the immediate future, any large quantities of low-temperature tar such as might result if a successful low-temperature carbonization process were developed, would have to be disposed of at fuel-oil prices and in direct competition with petroleum products.

The most extensive comparison of the analytical composition of various semi-commercial low-temperature tars from American plants, has been made by Davis and Galloway[79] of the Bureau of Mines. They obtained analytical data on 7 low-temperature tars, 1 coke-oven tar, and 1 water-gas tar. The tars were fractionated by the Standard Bureau of Mines method for the analytical distillation of petroleums. Tar acids, tar bases, unsaturated hydrocarbons, aromatic hydrocarbons, sulfonation residue, specific gravity, viscosity, and free carbon were determined.

Church,[80] employing the Standard Barrett Company methods for high-temperature tar, examined several samples of tars produced in the Parr-Layng low-temperature carbonization process. Representative over-all yields per ton of coal carbonized were 1.5 gallons of light oil, 5.1 gallons of No. 1 creosote, 1.6 gallons of tar acids, and 6.6 gallons of pitch. Owing to the somewhat higher temperature employed in the Parr process of carbonization, this tar was found to have some of the characteristics of high-temperature tar.

Burke and Caplan[81] found that the undesirable red color of aqueous extracts and emulsions of low-temperature tar is due to air oxidation of *o*-dihydrophenols which constituted approximately 0.8% of the tar studied. They extracted these compounds from 50 gallons of tar distillate, by two extractions with equal volumes of saturated aqueous $Na_2B_4O_7$ solution. The predominating compound identified was 3, 4- or 3, 6-dimethylcatechol.

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[78] Morgan, *Proc. Am. Gas Assoc.*, 1926, 1192.
[79] Davis and Galloway, *Proc. Am. Gas Assoc.*, **1925**, **887**.
[80] Church, *Ind. Eng. Chem.*, 19, 31 (1927).
[81] Burke and Caplan, *Ind. Eng. Chem.*, **19**, **34** (**1927**).

Motor fuel yields obtainable from low-temperature tar by pressure distillation are considerably lower than those obtainable from petroleum. Morrell and Egloff[82] report a maximum yield of 18.1% of 39° Baumé oil boiling over a range of 120-430°F. Cracking decreased the percentage of unsaturated hydrocarbons and increased the percentage of aromatics, naphthenes and paraffins. Neither primary amines nor $C_{10}H_8$ could be detected before or after cracking, although some anthracene was formed. The amount of tar acids was decreased slightly and appeared after cracking to consist mostly of cresols.

Purification of Manufactured Gas. Sperr,[83] in a recent review of progress in gas purification, has described the newer developments of The Koppers Company in liquid purification which have been installed in a number of plants in the last five years. The Seaboard process using 1 to 3% Na_2CO_3 solution is the simplest and most inexpensive of the liquid methods for removing hydrogen sulfide and hydrocyanic acid. With the necessary catch boxes it occupies small ground space in comparison with the equipment for complete oxide purification. It has one disadvantage in that the H_2S is removed from the solution by blowing air through it. This hydrogen sulfide laden air has sufficient odor to render it objectionable in the vicinity of residential districts. To meet these disadvantages and to provide a means for recovering sulfur in salable form, and to accomplish complete instead of partial purification, The Koppers Company is now installing what is known as the Sulfur Recovery Process.[84] There are two forms of this process, one being used for coal-gas purification and the other for the treatment of water gas and other gases containing substantially no hydrocyanic acid. The basic principles of the first were developed by Mann and Lebo of the Standard Development Company.[85] The second is a catalytic process developed by the Pacific Gas and Electric Company at San Francisco. The apparatus employed is nearly the same in both cases. Briefly, the first process is based on the absorption of H_2S in 0.5 to 2% Na_2CO_3 having an iron compound in suspension. The sulfide-containing solution is then subjected to the action of finely atomized air which revivifies the purifying medium, liberates free sulfur and separates the free sulfur by flotation. Other references to proposed processes for the removal of raw hydrogen sulfide by liquid treatment are confined to the patent literature.[83] For the removal of carbon disulfide from gas, Weiss [86] proposes scrubbing with aniline or other organic amines in aqueous solution. That organic sulfur compounds as well as H_2S poison metal oxide catalysts in the reduction of steam by carbon monoxide was shown by Evans and Newton.[87] Hence, water gas for hydrogen production must be completely purified with respect to all sulfur compounds.

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[82] Morrell and Egloff, *Ind. Eng. Chem.*, **17**, 473 (1925).

[83] Sperr, Recent Progress in Science in Relation to the Gas Industry, Chapt. IX (1926).

[84] Sperr, *Gas J.* (London), **175**, 262 (1926).

[85] Mann and Lebo, U. S. P. 1,525,140 (Feb. 3, 1925).

Naphthalene removal by scrubbing the gas with petroleum oil is quite effective and according to tests by Kohr [88] has no appreciable effect on the heating value of the gas.

Sperr [89] has contributed a valuable analysis of the technical and economic factors involved in the dehydration of manufactured gas by various chemical and physical methods including refrigeration, use of solid and liquid chemical absorbents, and physical absorbents. Dehydration of manufactured gas is a subject that is being given serious consideration as a possible means of eliminating to a large degree the internal corrosion of gas-distribution equipment.

Considerable progress has been made in recent years in the practical application of the Cottrell electrical precipitation process to the de-tarring of gases and the removal of solid suspended matter. Sultzer [90] of The Research Corporation has reported the installation of about 30 units at various gas plants during the last two years.

Combustion in Gas Burners. Haslam and associates at the Massachusetts Institute of Technology have made an experimental study of the mechanism of gaseous combustion in burners.[91]

Luminous flames.—Haslam and Boyer [92] studied the radiation from luminous flames of four gases –namely, city gas, methane, ethylene, and acetylene—by allowing the radiation from a small flame to fall on a thermopile at such a distance from the flame that it could be considered as a point source. They obtained values of 9.2, 8.0, and 10.65% of the total heat of combustion, respectively, for city gas, methane, and ethylene. They considered these values low, because of the difficulty of obtaining complete luminosity in such a small flame. However, acetylene gave a truly luminous flame, radiating 28.2% of the total heat of combustion as compared with 6.9% for a similar non-luminous acetylene flame. Haslam believes that engineers have not fully appreciated the full possibility of using luminous flames in heating appliances.

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[86] Weiss, U. S. P. 1,549,426 (Aug. 11, 1925).
[87] Evans and Newton, *Ind. Eng. Chem.*, 18, 518 (1926).
[88] Kohr, *Gas Age-Record*, 57, 187 (1926).
[89] Sperr, *Chem. Met. Eng.*, 34, 97 (1927); *Am. Gas J.*, 125, 633, 638, 651 (1926).
[90] Sultzer, Recent Progress in Science in Relation to the Gas Industry, Chapt. VII (1926).
[91] Rembert and Haslam, *Ind. Eng. Chem.*, 17, 1233, 1236, 1238, 1240 (1925).
[92] Haslam and Boyer, *Ind. Eng. Chem.*, 19, 4 (1927).

In the manufacture of carbon black by the incomplete combustion of natural gas, luminous flames from slotted lava-tipped burners are allowed to impinge on cold metal surfaces. Chamberlin and Thrun[93] at Lehigh University studied the size and shape of these flames by photographic methods, with reference to the size of the slots, and the pressure and rate of flow relations.

That insufficient primary air and incomplete combustion produced luminous flame, has been known for many years, but no one imagined that CaO and other very refractory oxides could be melted rapidly in a flame of atomic hydrogen with no oxygen present. Langmuir,[94] of the General Electric Company laboratory at Schenectady, again startled the technical and scientific world at the Philadelphia meeting of the American Chemical Society in September, 1926, with an extremely interesting account of the dissociation of molecular hydrogen at high temperatures produced by passing it through a tungsten arc. If this atomic hydrogen is then allowed to re-associate on the surface of refractory materials or metals, the heat developed is high enough to melt them; and in case of metals, the strongly reducing atmospheres aid in welding, as in the case of aluminum and its alloys. Langmuir has calculated the temperature of the atomic hydrogen flame at 4030°K, as compared to 3270°K for acetylene burning with an equal volume of air. Torches have been developed for the practical application of atomic hydrogen flames to the welding of metals, where it has a useful field not only for iron and its alloys, but for such metals and alloys as contain aluminum, magnesium, chromium, manganese, etc.

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[93] Chamberlin and Thrun, *Ind. Eng. Chem.*, 19, 752 (1927); *Gas Age-Record*, 57, 41 (1926).

[94] Langmuir, *Gen. Elec. Rev.*, 29, 153, 160 (1926); *Ind. Eng. Chem.*, 19, 667 (1927).

Production and Use of Mixed Gases. According to Conner,[95] director of the Testing Laboratory of the American Gas Association, "One of the most vital problems confronting the gas industry today is that of mixing gases of different specific gravities and different heating values so that a gas of sufficiently uniform quantity will be secured for satisfactory appliance operation."

Weaver [96] of the U. S. Bureau of Standards has contributed a critical review of the relation between heating value of a gas and its usefulness to the consumer, based on a consideration of direct determination in various appliances, and statistics from communities before and after changes in heating value. In his opinion the data from both classes lead to the conclusion that usefulness is accurately proportional to heating value.

Perry [97] of the United Gas Improvement Company has contributed a timely and valuable analysis from an engineering and economic point of view, of the types of plants and quality of gas best suited for the development of the gas industry. He recommends the use of a base load gas of 440 B.t.u. per cu. ft. heating value, made up of coal gas plus producer gas, and as a peak-load gas a lightly carburetted water gas of the same heating value. Use of all the coke from the coal gasification for making peak-load gas would give a total mixture of about 34% base-load gas and 66% peak-load gas, whereas up to 75% of such peak-load gas can be used without burner difficulties.

The available data on blending natural and manufactured gas and on lowering the heating value of natural gas by cracking have been summarized by Wright.[98]

Natural gas technologists will find a valuable group of papers covering some 200 pages in the Natural Gas Number of The Oil and Gas Journal for June 16, 1927. These papers cover geology, drilling, and distribution and utilization of natural gas. Logan in three papers discusses the soil corrosion experiments of the Bureau of Standards. Garner covers recent developments in the recovery of gasoline from natural gas; Carr gives a résumé of the carbon-black industry, and Moore traces the development of the government helium plant from its initiation in 1917 when the cost of helium was $1500 a cubic foot to the present time when it is being produced for 4.5 cents a cubic foot.

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[95] Conner, *Am. Gas Assoc. Mo.*, 9, 199 (1927).

[96] Weaver, Bur. Standards, Tech. Paper no. 290 (1925).

[97] Perry, *Proc. Am. Gas Assoc.*, 1925, 818.

[98] Wright, Recent Progress in Science in Relation to the Gas Industry, Chapt. XIV (1926).

The chemical composition and physical properties of various natural gases, with methods of sampling and analysis, are ably covered by Garner and Miller.[99]

Analytical Methods and Tests. In the field of general gas analysis two bulletins have recently been published; one describing the present form and manipulation of the Bureau of Mines [100] type of Orsat apparatus for gas analysis, and the other describing the apparatus and methods used for the analysis of fuel gases at the University of Illinois.[101] Parr [102] has also developed a recording gas calorimeter of the flow type.

For the continuous determination and recording of very small concentrations (as low as 0.001%) of carbon monoxide in air, the Bureau of Mines [103] has developed an instrument in which the gas to be analyzed passes through a cell containing a number of differential thermocouples in series and a "hopcalite" catalyst for oxidizing the CO. The temperature rise is recorded on a potentiometer. This apparatus has been successfully operated for more than six months in the Liberty Tunnels of Pittsburgh for controlling the ventilation and preventing accumulation of CO from the automobile exhaust gases.[104]

Another important advance in methods for determining small concentrations of CO is the development of a simple portable outfit by Sayers and Yant [105] for the determination of small percentages (0.01 to 3%) of CO in air or the percentage saturation of the blood with CO, by a colorimetric method involving the addition of pyrogallic and tannic acids to dilute solutions of blood. This outfit is very useful in the diagnosis and investigation of carbon monoxide poisoning.

Huff [106] has worked out the proper conditions for applying the cupric xanthate method to the quantitative determination of small amounts (1 mg. or less of CS_2 in 100 c.c. of gas) of carbon disulfide in coal gas.

[99] Garner and Miller, *Oil Gas J.*, 25, 137 (1927).
[100] Fieldner, Jones and Holbrook, Bur. Mines, Tech. Paper no. 320 (1925).
[101] Parr and Vandaveer, Univ. Ill.. Expt. Sta. Circ. no. 12 (1924).
[102] Parr, *Ind. Eng. Chem.*, 18, 1194 (1926).
[103] Katz, Reynolds, Frevert and Bloomfield, Bur. Mines, Tech. Paper no. 355 (1926).
[104] Fieldner, Katz and Meiter, *Eng. News-Record*, 95, 423 (1925).
[105] Sayers and Yant, Bur. Mines, Tech. Paper no. 373 (1925).
[106] Huff, *J. Am. Chem. Soc.*, 48, 81 (1926).

New Processes of Interest to the Gas Industry. Haslam,[107] and Fieldner and Brown [108] have contributed reviews of new processes that are of interest to the gas and coal industry, the most important being the following:

1. The manufacture of liquid fuels from gas or coal and its relation to catalytic enrichment of blue gas, including under this head the pressure synthesis of methanol [109] and synthol [110] from water gas, the atmospheric synthesis of hydrocarbons [111] from water gas and the hydrogenation and liquefaction of coal.[112]
2. The cracking of oil for the conjoint production of motor fuels and enriching gases.[107]
3. The development of small portable gas units for isolated homes.[107] Charcoal gas-producers and liquefied propane tanks are both coming into use.

No American research work on methanol synthesis or hydrogenation of coal has been published up to the time of preparing this report, although two years of intensive research and experimental work by Lazote, Inc., has resulted in the development of a new and purely American process, radically different from and an improvement on the foreign processes.[113] The new methanol plant is operated in conjunction with Lazote's synthetic ammonia plant, thus serving to remove the CO from the hydrogen-containing gases. The operations of the experimental plant are reported so successful that plans have been drawn to allow for plant expansion sufficient to meet the entire American demand for methanol. This combination of ammonia and methanol synthesis is another example of the economic advantages of large-scale chemical manufacturing organizations with adequate research facilities. From a recent study of the writer it does not seem profitable to utilize the off-peak water-gas capacity of gas plants for methanol production; [114] neither is it economical, according to Dodge [115] to liquefy coke-oven gas solely for the production of hydrogen for ammonia synthesis, although if at the same time light oils and ethylene are abstracted from the gas, it might be made to pay.

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[107] Haslam, Recent Progress in Science in Relation to the Gas Industry, Chapt. VI (1926).

[108] Fieldner and Brown, *Blast Furnace and Steel Plant,* **14**, 138, 148 (1926); *Ind. Eng. Chem.*, **18**, 1009 (1926).

[109] Patart, International Conference on Bituminous Coal, p. 132 (1926).

[110] Fischer, *Ind. Eng. Chem.*, **17**, 574 (1925).

[111] Fischer, International Conference on Bituminous Coal, p. 234 (1926).

[112] Bergius, International Conference on Bituminous Coal, p. 102 (1926).

[113] *Ind. Eng. Chem.*, News Ed., **5**, no. 7 (1927).

[114] Fieldner, *Am. Gas J.*, **126**, 179 (1927).

[115] Dodge, *Chem. Met. Eng.*, **33**, 416 (1926).

Utilization of Natural Gas. The recent merger of the Natural Gas Association with the American Gas Association, which has heretofore concerned itself with manufactured gas, is a progressive step that will result in mutual benefit to both industries. It makes available the new testing laboratory of the Association at Cleveland for the development of better gas appliances, and facilitates a joint research program on the development of efficient gas appliances for the utilization of gas in industry for which $500,000 has been appropriated. Also the research on mixed gases, to which reference has been made earlier in this chapter, is of interest to both industries.

Aside from direct use as a fuel, natural gas is an important source of gasoline, obtained by compression or absorption processes. Radical improvements in fractionation towers have led to sharper separation of the different constituent hydrocarbons so that large quantities of propane and propane-butane mixtures are now available for industrial use. These are sold in tanks under pressure for fuel purposes, including small tanks for supplying domestic stoves and also railroad tank cars which supply town gasworks.

Problems in Coal Research

Research on the constitution of coal in relation to its origin and utilization is of fundamental importance. Information gleaned in this field of investigation is useful to the geologist in the classification of coal, to the gas engineer in the selection of coals for gas manufacture, to the combustion engineer in affording a better understanding of the burning and caking properties of the coal on the grate, and to the chemical engineer in the selection of coal as raw material for chemical products. Research on the constitution of coal requires investigators of the highest training in organic and physical chemistry and must have the close cooperation of paleobotanists and geologists who have made a specialty or life work of the study of coal. We are fortunate to have investigators of the latter type in America, and every effort should be made to secure for them stronger support in the widening of their sphere of influence either through cooperation with university investigators or the support of research associateships working under their direction. Following is a brief outline of the type of problems to be worked on under a study of the constitution of coal. Acknowledgments are due to Dr. David White of the National Research Council for the greater part of this outline.

Constitution of Coal

A. *Paleontological Studies:*
  I. Origin.
  II. Transformation.

III. Structure.
IV. Present condition of constituents.

The examination of thin sections of coal by transmitted light, and of polished and etched sections of coal would form a major part of these studies which would include discrimination of bark, cuticle, wood, pith, epidermis, etc., and determination of their proportions in the fusain, the dull laminae, and the bright lenses and streaks of different coals of different ages, and of slightly different depositional types.

B. *Physico-Chemical Studies:*

I. Micro-chemical Studies.

(a) A study of selective action of solvents and reagents on thin sections and polished surfaces of coal at room temperature in order to observe under moderately high powers of the microscope the chemical actions on different kinds of debris and ulmic detrital matter and colloidal material making up coal.

(b) A study of effect of heat and observations of changes of state of fossil constituents as the temperature is raised under close control in a furnace under a microscope. White and Stadnichenko have developed such a furnace and are now making such a study of oil shale. A similar study directed toward coal would make it possible—

1. To learn the temperatures at which the different fossil commodities volatilize or undergo transformation.
2. To make great progress in the recognition of chemical distinction in the composition of the various visible physical constituents of the coal as those differences are reflected by changes of state at different temperatures.

It would also be of high value if an apparatus could be worked out for collecting the gaseous products of distillation that come off from the coal when heated in the micro-furnace at definite temperatures at which certain constituents are observed to change in state—that is, it might be possible to develop a micro-retort with which the products yielded by the different commodities in the coal and their temperatures of transformation could be determined. Through the effect of heat, solvents and reagents upon recognizable constituents of the coal, we should be able to make some progress in the recognition of the nature of the chemical changes that take place in the different types of plant structure and plant products during carbonization.

(c) Effect of oxidation. The microfurnace could also be used for burning thin sections of coal to ashes and observing their distribution and possible catalytic effect on combustion and carbonization of the coal. The furnace could also be used for determining the effects of oxidation of coal at various temperatures beginning at room temperature and up through the range to the temperatures at which coal becomes plastic. A special study would be the effect of oxidation on the coking properties and determining, if possible, which identifiable constituent in the coal is most affected by such oxidation before retorting. The test chamber could be arranged so that the heating could be done in vacuo or in any desired atmosphere.

II. A study of the ulmic matter of coal.

(a) The relation between composition and oxidizability of coal with special reference to the relative oxidizing tendency of the ulmic portion of coals of different ranks ranging from lignite to anthracite. This might serve as a very useful basis for classification of coals and is undoubtedly a very important consideration in the control of the coking properties of coal.

(b) The microstructure of coal in relation to the ulmic matter and its degree of oxidation, following up especially the general change in structure and appearance of coals when subjected to changes due to regional metamorphism. The work should be closely correlated with that under (a) and the results would be very useful in the scientific classification of coal based upon their chemical and physical properties.

C. *X-Ray Studies:*

Investigation of the possibility of X-ray studies as an aid in fundamental studies on the constitution of coal.

D. *Study of Constitution of Primary or Low-Temperature Tar:*

Work thus far has covered the low boiling constituents and the simple phenols, but virtually nothing is known of the constitution of the complex high molecular weight phenols and tar acids that comprise a very large part of the tar. A knowledge of their constitution would aid in unraveling the constitution of coal itself.

Research on Manufactured Gas

Many problems could be cited in connection with manufactured gas, but probably none is more fundamental or of wider interest than the removal of organic sulfur compounds. It is recognized that the greater portion of organic sulfur is carbon bisulfide, but there is a wide difference of opinion, and virtually no quantitative data are available on these compounds, other than on carbon bisulfide. These should be identified and the amounts determined in order to furnish the basis for other research problems on the removal of organic sulfur compounds, as these are objectionable whether the gas is used for a fuel or for chemical synthesis.

Chapter XLII.

Petroleum Chemistry and Technology.

Benjamin T. Brooks

The chemistry and technology of petroleum has progressed a long way since 1890 when Burton went to Whiting, Indiana, and was asked if he had brought his "kit" with him. Like many other American industries, the petroleum refiners are not much given to publicity but the number of papers which have appeared in chemical and engineering journals in the last few years reflects a liberal attitude toward such publication on the part of most of the larger companies. There is also abundant evidence that academic investigators are interested in petroleum to a greater degree than heretofore.

The correctness of Doherty's theory that the viscosity and surface tension of crude petroleum are very different underground when under very high natural gas pressure, due to the solution of the gas in the oil, has been proven. Beecher and Parkhurst [1] give the results of an investigation of the subject, which is of the greatest importance in view of the application of gas or air pressure in old oil fields, where the natural gas pressure has been lost, to increase the flow of oil. Very few outside the oil industry appreciate the fact that by the usual methods the total recovery of oil from a given field is only 20% to 25% of the total crude in the sand. In one of the old fields in Pennsylvania the method of flooding the sand with sodium carbonate solution is being tried with very satisfactory results. The possible economic importance of scientific investigations along these lines cannot be overestimated. Research men should see to it that they are not merely called upon to explain the accomplished fact.

Refinery engineers have frequently commented on the scarcity of physical data on American petroleums. Leslie [2] and his associates have determined experimentally the latent heats of vaporization of distillates from a typical high grade paraffin base petroleum (from Cabin Creek, W. Va.) and note that the values obtained, particularly those for the higher boiling fractions, fall well below those established by calculation from Trouton's rule. Fortsch and Whitman[3] have experimentally determined the specific heats of fifteen petroleums over the range 50-430°F.

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[1] *Nat. Pet. N.*, **18**, 72 (Oct. 20th, 1926).
[2] *Ind. Eng. Chem.*, **18**, 45 (1926).

Propane is being used as a refrigerant in the recovery of gasoline from gas, and propane and butane are now available in tank cars at substantially gas oil prices, no very important industrial use having been found for these hydrocarbons. The rectification of natural gas gasoline, now very generally practiced, permits the separation of propane or butane in very pure state. The industry is much interested in whether or not patents covering rectification of light gasoline will be sustained in pending litigation.[4]

The difficulty of preparing pure hydrocarbons from petroleum is shown by the work of Brown and Carr[5] who employed an eighteen foot column packed with small Raschig rings. From 135 gallons of gasoline small fractions of pure pentane, isopentane, isohexane, *n*-hexane, *n*-heptane, isooctane, *n*-octane and *n*-nonane were obtained. It is of interest to note that this gasoline, from a typical Appalachian paraffin base crude, yielded substantial proportions of isopentane, isohexane and isooctane, the latter in particularly large proportion. Nine fractionations gave 2 liters of *n*-heptane (98.6 to 98.7°C) and ten fractionations gave 2.5 liters of isooctane (117.9 to 118.1°C). The old fiction that "American" or "Pennsylvania" petroleum consists of a mixture of normal paraffins is gradually being dispelled. The aromatic hydrocarbon constituents of an exported American kerosene have been studied by Carpenter[6] who found about 11% by volume. Although aromatic hydrocarbons are almost universally present in kerosenes, the use of liquid sulfur dioxide for refining is used in this country only in California.

Paraffin wax, from Scotch shale, melting at 55-56°C has been separated into seven fractions of constant boiling point and shown by comparison with normal synthetic paraffins and by X-ray spectrum analysis to be normal paraffins,[7] confirming Krafft's conclusion as to the character of such wax. An excellent paper by Buchler and Graves[8] gives the properties of waxes crystallized from ordinary paraffin wax, petrolatum wax, slop wax and rod wax. Petrolatum wax yielded a series of wax hydrocarbons from $C_{34}H_{70}$, melting point 71.0°C (159.7°F.) to $C_{43}H_{88}$ melting at 83.8°C (182.7°F.). From a study of the physical properties they conclude that all *petroleum waxes* belong to the straight chain series C_nH_{2n+2}. They have cleared up a great deal of confusion regarding the nature of these higher melting point waxes and also shown that the separation of soft wax causes the higher melting point wax to separate in needles instead of plates, and, in excessive amounts, leads to an amorphous or microcrystalline appearance. The nature of vaselines is accordingly clear. As so often happens when such a thorough scientific investigation is made, an industrial product results, in this case a wax melting at 74°C and evidently of superior value for electrical insulation purposes.[9] Padgett, Hefley and Henriksen[10] have also studied the crystallizing habit of the paraffin waxes. The advantages of using nitrobenzene and acetone as solvents for determining wax in oil-wax intermediates has been shown by Henderson and Ferris.[11]

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[3] *Ind. Eng. Chem.*, 18, 795 (1926).
[4] *Nat. Petroleum News*, 19, No. 23, 23 (1927).
[5] *Ind. Eng. Chem.*, 18, 718 (1926).
[6] *J. Inst. Petrol. Tech.*, 12, 518 (1926).
[7] Piper, Brown and Dyment, *J. Chem. Soc.*, 127, 2194 (1925); Francis and Wood, *ibid.*, 1926, 1420.

The oxidation of paraffin wax and other hydrocarbons by air continues to be of interest. Francis and Gauntlett[12] have shown that commercial paraffin yields, as intermediate products, secondary alcohols and ketones, the ketone oxygen being on the third or fourth carbon atom. The proportion of non-acidic products rapidly diminishes as acids are formed. The Penniman process employs air under pressure and the process is carried out to give a series of oxidation products including some of the simpler aldehydes, ketones and acids, and is reported to be applied to a variety of oils. James[13] has studied the partial oxidation of petroleum oils in the presence of a catalyst.

Very little can be said regarding the technology of petroleum in a brief review, but Leslie and Good[14] have made a comparative study of equilibrium single flashing and equilibrium successive flashing. Single flashing is superior to successive flashing as regards yield of distillate, exhaustion of residuum, composition of

[8] *Ind. Eng. Chem.*, 19, 718 (1927).
[9] Lee and Lowry, *Ind. Eng. Chem.*, 19, 302 (1927).
[10] *Ind. Eng. Chem.*, 18, 832 (1926).
[11] *Ind. Eng. Chem.*, 19, 262 (1927).
[12] *J. Chem. Soc.*, 1926, 2377.
[13] U. S. P. 1,597,796-1,597,798 (Aug. 31, 1926).
[14] *Ind. Eng. Chem.*, 19, 453 (1927).

vapor, and heat requirement. "Worst of all is differential vaporization or batch distillation, the limiting process of successive flashing. Yet, in practice, batch distillation is still used by many of the largest refiners. Also still batteries, operated continuously, and representative of differential incremental vaporization, are widely used as a preferred type of equipment." Single equilibrium flash is obtained in pipe still practice and this method combined with properly designed bubble towers makes an operation incomparably more efficient than old fashioned batch distillation. Yet, as Leslie and Good point out, archaic batch stills continue in use and even new ones are being installed today. Periods of economic distress in the petroleum industry are probably necessary in order that engineers and chemists may have opportunities to correct such venerated but sorry practices.

Cracking processes have been much improved in the last two years, particularly with respect to the daily throughput and gasoline production per unit. Leslie and Potthoff [15] have made a study of the thermal relationships and estimate that the endothermic cracking reactions absorb about 900 B.t.u. per pound of gasoline produced. They also discuss the effect of removing gasoline during the cracking. They were able to employ long reaction time at nearly constant temperature (800° F.) by permitting the escape of gas and volatile products, otherwise constant pressure and temperature under cracking conditions could not be maintained. They have confirmed earlier results [16] to the effect that increase of pressure decreases the percentage of olefins in the gasoline as indicated by the sulfuric acid reaction. They also show that olefins are condensed at 800° F, the percentage of olefins decreasing with increased time of heating. Diolefins are evidently condensed fairly rapidly at the lower temperatures prevailing in gasoline bubble towers at moderate pressures.[17] DeFlorez [18] has noted the cumulative benefits of automatic temperature regulation of cracking processes, and Auld and Dunstan [19] have stated that the deposition of coke in liquid phase cracking processes can be almost entirely obviated by close temperature control. There is also considerable evidence that complex aromatic hydrocarbons are chiefly the coke forming substances [20] and their removal from recycle stock by

[15] *Ind. Eng. Chem.*, **18**, 776 (1926).
[16] Brooks and others, *Ind. Eng. Chem.*, **7**, 180 (1915).
[17] Brooks, *Ind. Eng. Chem.*, **18**, 1198 (1926; *cf.* Sachanen, *Petr. Z.*, **1927**, 521.
[18] *Am. Inst. Min. Met. Eng.*, Annal Report on Petroleum Technology, **1926**, 410.
[19] *Ind. Eng. Chem.*, **18**, 803 (1926).
[20] Brooks, *Ind. Eng. Chem.*, **18**, 527 (1926).

sulfuric acid or liquid sulfur dioxide has been proposed in order to prolong the cracking operation period, between coke cleanouts. An excellent general review of the subject of cracking has been given by Delbridge.[21]

Cracking in the vapor phase at high temperatures to produce a highly unsaturated gasoline of very valuable anti-knock properties is being tried out by several companies on an industrial scale. Such cracked gasoline costs more to produce than that produced by the so-called liquid phase processes but serves as useful material for blending.

That even the saturated paraffin hydrocarbons have very different anti-knock values has been shown by Edgar,[22] who has proposed that mixtures of normal heptane and 2,4,4-trimethylpentane be used for rating the anti-knock value of commercial motor fuels. The very pronounced differences in the anti-knock properties of various straight run and particularly cracked gasolines made from different crudes give a practical bearing to the chemistry of such gasolines, which is as yet only very imperfectly known. Engine tests are still the most certain and accurate method of determining the anti-knock value of a motor fuel. Stevens and Marley[23] state, "As a result of chemical analyses and engine tests on eighteen gasolines, it would appear that the method evaluating motor fuels here considered has given results agreeing approximately with engine tests for about half of the fuels studied. The other gasolines examined showed rather wide discrepancies between the findings of analysis and engine test. It is not believed that the anti-knock value of gasolines can be satisfactorily determined by this method."

The method of catalytic dehydrogenation[24] does not appear to have been applied to the study of American gasolines of naphthenic type but there is some indication that this line of work has assumed an industrial aspect in Europe.[25]

The results of refining cracked gasoline, while in a vapor state, with fuller's earth have been described by Mandelbaum[26] and Nisson and Mitchel.[27]

Gum formation in cracked gasolines is one of the results of oxidation of the olefins by air, with the initial formation of peroxides and is a general property of olefinic hydrocarbons but the oxidation is rapid only with diolefins. The oxidation of sulfur compounds with the development of acidity of SO_2 or SO_3, even in traces, results in discoloration.[28] In the autoxidation of certain compounds of isothiocyanates with oximes the sulfur is oxidized to SO_2 and SO_3.[29] The oxidation of heavy oils by air in the presence of various inhibitors and catalysts has been studied by Haslam and Frölich.[30] Moureau, who has made an extensive study of oxidation inhibitors, has shown that tetraethyl lead is an oxidation inhibitor. The paraffin hydrocarbons show an autocatalytic autoxidation, preceded by a period of induction, which is suppressed by certain substances. The formation of peroxides is noted and Moureau and his co-workers [31] incline to the peroxide theory of suppressing engine knock proposed by Callendar [32] and state that anti-detonants exert their effect by preventing the formation of peroxides.

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[21] *J. Franklin Inst.*, 202, 569 (1926).

[22] *Ind. Eng. Chem.*, 19, 145 (1927).

[23] *Ind. Eng. Chem.*, 19, 228 (1927); *cf.* Egloff and Morell, *ibid.*, 18, 354 (1926); Brame et al, *J. Inst. Petr. Tech.*, 12, 48 (1926).

[24] Zelinsky, *Ber.*, 59, 2580 (1926).

[25] *I. G. Farb. Akt. Ges.*, Brit. Pat. 261,393 (1927).

[26] *Ind. Eng. Chem.*, 18, 564 (1926).

[27] *Nat. Petr. News*, 19, 90 (Apr. 27, 1927).

The theory of the action of detonation inhibitors and inducers has been the subject of a series of papers. A comprehensive review of the subject is beyond the limitations of the present paper, but particular mention should be made of the work of Charch, Mack and Boord [33] which offers experimental evidence supporting their explanation which is based on the chemical properties of the various materials affecting detonation. Lind and Bardwell [34] have studied the effect of selenium diethyl on the oxidation of methane by oxygen at ordinary temperature under the ionizing influence of radon. "It appears to be generally conceded at present that ionization does not play a primary role in explosive reaction or flame propagation.[35] It has been shown here that in the ionized oxidation of methane the presence of an anti-knock does not retard but rather accelerates the reaction, probably by taking part in it through enhancing the absorption of the energy of alpha-radiation. . . . The writers are not aware that any direct evidence exists that the anti-knock does actually reduce the velocity of flame propagation." Their results are rather more in accord with the theory of Charch, Mack and Boord, that it does the opposite by facilitating and in making the initiation of flame more instantaneous and uniform. In a more recent paper by Lovell, Coleman and Boyd [36] it is shown that "when the engine knocks, whether the detonation is caused by the presence of kerosene in the gasoline or by a chemical knock inducer, the gasoline burns at a rate more rapid than normal. . . . The presence of tetraethyl lead in a knocking combustion brings the rate of burning back to normal." Clark and Henne [37] have made a study of the ultraviolet spectroscopy of engine fuel flames. In a series of papers Brown and Watkins [38] have shown the importance of the autoignition temperature of the fuel employed, and the rate of rise of pressure. Brown also distinguishes between engine knock and a true detonation wave such as occurs in progressive homogeneous reactions. "The rate of flame travel and the rate of rise of pressure in the explosions following autoignition may approach the rates accompanying the detonation wave, but the mechanism of autoignition is so radically different from the mechanism initiating the detonation wave that a precise distinction should be made."

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[28] Brooks, *Ind. Eng. Chem.*, **18**, 1198 (1926).
[29] Gheorghiu, *Bull. Soc. chim.*, **41**, 50 (1927).
[30] *Ind. Eng. Chem.*, 19, 292 (1927).
[31] *C. R.* 184, 413 (1927); *La Rev. Petrol.*, 1926, Oct. 16, p. 25.
[32] *Engineering*, 123, 147 (1927).
[33] *Ind. Eng. Chem.*, 18, 334 (1926).
[34] *Ind. Eng. Chem.*, 19, 231 (1927).
[35] Symposium of the Faraday Society on "Explosive Reactions in Gaseous Media," June, 1926.

The question of the per cent of sulfur which a motor fuel may contain without injury to automobile engines has been much discussed. The advisory board of the American Petroleum Institute and Committee D-2 of the American Society of Testing Materials recently voted down the proposal that the federal specification board be asked to raise the sulfur limit from 0.1 to 0.15%. The large refining losses resulting from removing sulfur, probably in the form of thiophenes, from certain cracked gasolines, have been pointed out by Egloff.[38a] The chemistry of the sulfur compounds of petroleum is being actively investigated under the American Petroleum Institute research program. It is of interest to note that the constitution of the thiophanes, discovered many years ago by Mabery and Quayle,[39] has been confirmed and Thierry [40] has isolated tetra- and pentamethylene sulfides from Persian oil and Challenger [41] has found them, together with a series of thiophenes, in Kimmeridge shale oil. Silica gel is not very effective in removing sulfur compounds from gasoline.[42]

[36] *Ind. Eng. Chem.*, **19**, 373 (1927).

[37] *J. Soc. Automotive Eng.*, **20**, 264 (1927).

[38] *Ind. Eng. Chem.*, **19**, 363, 366 (1927).

[38a] A. I. M. E. Annual Rept. on Petroleum Technology, **1926**, 385.

[39] *Am. Chem. J.*, 35, 404 (1906).

[40] *J. Chem. Soc.*, **127**, 2756 (1925).

[41] *J. Inst. Petr. Techn.*, **12**, 106 (1926); Scheibler, *Z. angew. Chem.*, **39**, 1397 (1926).

[42] Waterman & Tussenbroek, *Brennstoff-Chem.*, **8**, 20 (1927).

Trusty, Wood and Sheely [43] give the comparative results of various industrial refining methods as regards removal of sulfur compounds, and Faragher, Morrell and Monroe [44] have shown that the percentages of sulfur as hydrogen sulfide, elementary sulfur, mercaptans, sulfides, disulfides and residual sulfur can be quantitatively determined. The advantages of treating with sulfuric acid at 12-20°F. have been pointed out by Klemgard.[45]

Corrosion of distillation equipment by hydrochloric acid can be largely overcome by ammonia,[46] but corrosion of cracking apparatus is believed to be due mainly to hydrogen sulfide which is formed during the cracking operation from sulfur derivatives in the oil. The relative resistance of various metals to hydrogen sulfide corrosion under refinery conditions has been given by Schmidt.[47]

Commercial processes for the distillation of lubricating oils under much higher vacuum than former practice have been developed.[48] Mabery [49] has examined lubricating oil fractions, separated by means of solvents, from Appalachian, Mid-Continent, Gulf Coast, Wyoming and Lima crudes. In view of the prevalent misconception as to the nature of the paraffin base crudes it is worth while to note, "The series C_nH_{2n}, the naphthenes, . . . do not appear in any of the (lubricating) oils examined in this laboratory. The hydrocarbons of this series seem to disappear in the separation of the lighter portions of the crude oils. The first series with lubricant quality in American petroleum is C_nH_{2n-2}, which forms a large part of the light lubricants in Appalachian oils and is also a constituent of most of the lighter crudes in other territory. Of the heavier series, the one most frequently present in light and medium heavy crudes is C_nH_{2n-4}. But the general lubricants, especially of the heavier grades, are the hydrocarbons of the series C_nH_{2n-8}. They represent the heavy lubricant constituents of all Appalachian oil, and are the principal representatives of lubricant quality in the Mid-Continent fields. . . . Hydrocarbons of the next series C_nH_{2n-10}, C_nH_{2n-12}, C_nH_{2n-14}, C_nH_{2n-16} and C_nH_{2n-18} also possess lubricant quality. . . ." We are entirely without any information as to the structure of these hydrocarbons. It is evident that they are polycyclic.

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[43] *Ind. Eng. Chem.*, **18**, 169 (1926).
[44] Presented at Richmond meeting, A. C. S.—April, 1927.
[45] *Ind. Eng. Chem.*, **19**, 539 (1927).
[46] *Chem. Met. Eng.*, 33, 628 (1926).
[47] *Petr. Z.* 22, 1139 (1926).
[48] Schulze, U. S. P. 1,448,709 (Mar. 13, 1923); Parish, *J. Franklin Inst.*, **203**, 781 (1927); Brooks, *Ind. Eng. Chem.*, **18**, 789 (1926).
[49] *Ind. Eng. Chem.*, **18**, 814 (1926); **19**, 526 (1927).

The lubrication symposium at Tulsa in April, 1926, under the direction of R. E. Wilson brought out extensive discussion of the lubrication of full and partial bearings,[50] oil flow in plain bearings,[51] fluid film lubrication and measurement of film thickness,[52] Diesel engine lubrication,[53] and a paper by Wilharm,[54] discussed the property of oiliness and gives a method of measuring this property. Moore and Barrett[55] state that the importance of oiliness in a lubricant is not great except where bearing pressures are very high or where the bearing surfaces are not adequate for the load. They compared the resistance of various commercial oils to air oxidation. Work of this character, comparing oils made from various crude petroleums, loses much of its value by not taking into account the refinery process history of the oils. The value of mechanical tests and the difficulty of rating oils on the basis of the usual chemical and physical tests have been pointed out in a valuable paper by Marshall and Barton.[56] They state that by the addition of fatty oils, "the increased oiliness of the oil was much more than offset by the increased carbonization (in internal combustion engines). . . . The use of cylinder stock in motor oils must be carefully controlled, especially in the case of oils for air cooled engines; it flattens the viscosity curve, reduces the oxidation figure, and generally improves the oil from the popular specification point of view, but in service produces carbon, and can even lead to lubrication failure."

A great deal has been published in the last year on the possibility of producing motor fuel by the low temperature carbonization of coal, by the hydrogenation of coal and by hydrogenation of carbon monoxide. The maximum possible amount of motor fuel obtainable even by the most widespread low temperature carbonization of coal, on the basis of the yields reported, can never be anything more than a very minor auxiliary of our motor fuel requirement, now amounting to about twelve billion gallons annually. The hydrogenation of coal, developed by Bergius, and the reduction of carbon monoxide by Patart and by Fischer, have had a

[50] Howarth, *Ind. Eng. Chem.*, **18**, 453 (1926).
[51] Barnard, *Ind. Eng. Chem.*, **18**, 460 (1926).
[52] Becker, *Ind. Eng. Chem.*, **18**, 471 (1926).
[53] Scott, *Ind. Eng. Chem.*, 18, 477 (1926); Norton and Matthews, *ibid.*, **18**, 480 (1926).
[54] *Ind. Eng. Chem.*, **18**, 463 (1926).
[55] *Petroleum Times*, **16**, 963 (1926).
[56] *J. Soc. Chem. Ind.*, **46**, 130T (1927).

great deal of publicity, to which only reference can be made here.[57]

The chemical utilization of petroleum has made progress in the industrial manufacture of amyl alcohols from pentane,[58] and Burrell has noted the effect of charcoal in improving the yield of amyl acetate from chloro-pentanes.[59] The manufacture of isopropyl alcohol from petroleum still gas by absorption of the propylene in 97% sulfuric acid at 25° has been described[60] and the manufacture of secondary and tertiary alcohols from the lighter hydrocarbons resulting from vapor phase cracking has been carried out on an industrial scale.[61] The manufacture of ethylene glycol and ethylene dichloride,[62] made from ethylene, is being carried out on a large industrial scale. The synthesis of rubber from dienes made from petroleum has long been regarded as a possibility. Certain aspects of the question of synthetic rubber are discussed by Geer[63] and Weil,[64] who hold out little promise for the success of such a synthesis.

The trend of research, at least along technical lines, is indicated in the present review. The chemical and physical researches which have been started under the plan of financial support provided for by the joint contributions of John D. Rockefeller, Sr., and the Universal Oil Company include a number of subjects of general scientific interest. The field of scientific research relating to hydrocarbon chemistry is so large that to list a few problems would be incongruous. In a broad sense, the strictly scientific side of petroleum chemistry includes a large part of the whole field of organic chemistry. For example, some of the researches recently provided for by grants from the American Petroleum Institute include the chemistry of nitrogen bases occurring in petroleum, another, the chemistry of sulfur derivatives; another, the chemistry of cyclopentanes, the effect of electric discharge upon gaseous hydrocarbons, investigation of thermolabile hydrocarbons, and the relative rates of reaction of the olefins. There are many indications that although heretofore most of the research on theoretical hydrocarbon chemistry has been done in Russia from now on most of this work will be done in America, side by side with technical work in one of America's greatest industries.

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[57] King, *J. Soc. Chem. Ind.*, 46, 181T (1927); Patart, Brit. Pat. 247,178 (Feb. 7, 1927); Oil produced by Bergius process, Heyn and Dunkel, *Brennstoff-Chem.*, 7, 81 (1926); Spilker & Zerbe, *Z. angew. Chem.*, 39, 1138 (1926); Skinner and Graham, *Fuel*, 6, 74 (1927); Fischer, *Nat. Petroleum News*, 18, No. 47, 49 (1926).

[58] Kirkpatrick, *Chem. Met. Eng.*, 34, 276 (1927).

[59] Koch and Burrell, *Ind. Eng. Chem.*, 19, 442 (1927).

[60] *Oil Gas J.*, 25, No. 36, 138 (1927).

[61] Davis and Murray, Brit. Pat. 248,375 (Feb. 24, 1925).

[62] Killeffer, *Ind. Eng. Chem.*, 19, 636 (1927).

[63] *Ind. Eng. Chem.*, 18, 1136 (1926).

[64] *Ind. Eng. Chem.*, 18, 1174 (1926).

Chapter XLIII.

Rayon.

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In reviewing progress in the American rayon industry one is confronted by a comparative scarcity of published information on the part of American investigators bearing upon chemical fundamentals underlying the four processes in use today. European investigation, both pure and applied, continues prolific, measured in terms of domestic researches. Manufacturers in this country, however, are annually spending large sums for research and development work, the results of which have been unquestionably reflected in a steady improvement in quality of rayon yarns. With the United States holding the lead over all countries in point of production, and with a growing activity on the part of industrial research organizations, it would be expected that the future should see this country more strongly fortifying its future position in this rapidly growing industry.

Production. The two outstanding commercial features during the past year have been an increase in quantity production with the United States still a world leader, and a steady decrease in price of the finished yarn, which has resulted in its introduction into many new fields of usefulness. The tables below present the salient points in respect to the growth of the industry.

Table 1. U. S. and World Rayon Production by Years.[1]

Year	*World-Pounds*	*United States-Pounds*
1920	50,000,000	9,000,000
1921	65,000,000	18,000,000
1922	79,738,000	26,000,000
1923	97,000,000	35,500,000
1924	141,164,000	38,750,000
1925	185,000,000	52,200,000
1926	*210,000,000	62,575,000

* Estimated.

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[1] Woolf, *Textile World*, 71, 813 (1927).

Table 2. Rayon Price History—1920-1926.[2]

Dates indicate period during which price was in force.

Date	*Period*	*Price 150 Denier "A"*	*Net Change*
Feb. 1920–May 1920.........	3 months	$5.90	$ . . .
May 1920–Oct. 1920.........	5 "	4.00	1.90
Oct. 1920–Oct. 1921.........	12 "	2,15	1.85
Oct. 1921–Feb. 1924.........	28 "	2.80	+.65
Feb. 1924–July 1926.........	29 "	2.00	.80
July 1926–Nov. 1926.........	4 "	1.65	.35
Nov. 1926–Mar. 1927.........	4 "	1.45	.20
Mar. 1927—to date.........	....	1.50	+.05

Table 3. Domestic Rayon Production by Manufacturers.

Company	*Process*	*1925-Lbs.*	*1926-Lbs.*	*1927-Lbs. Estimated*
The Viscose Company.......	Viscose	35,000,000	37,000,000	40,000,000
Du Pont Rayon Company....	Viscose	6,800,000	10,900,000	14,000,000
Tubize Artificial Silk Company	Nitro-cellulose	5,200,000	7,000,000	8,000,000
Industrial Rayon Corporation	Viscose	2,250,000	3,400,000	3,600,000
American Cellulose and Chemical Company	Cellulose Acetate	1,500,000	2,500,000	3,500,000
Belamose Corporation	Viscose	675,000	875,000	1,400,000
Acme Rayon Corporation....	Viscose	325,000	325,000	500,000
Other Firms		500,000	500,000	2,500,000
Total		52,250,000	62,250,000	73,500,000

Table 4. Rayon Production by Countries—1926.[3]

Country	*1926 Production Pounds*
United States	62,575,000
Italy	35,000,000
Germany	26,000,000
Great Britain	25,500,000
France	17,500,000
Holland	13,500,000
Belgium	13,100,000
Switzerland	8,000,000
Japan	5,500,000

Recently a new plant using the cuprammonium process has been put into operation by the American Bemberg Corporation, at Johnson City, Tennessee. The rated capacity of this plant is one and one half million pounds annually. It is the only American plant at the present time using this process. Additions or new units have been added by several of the older companies.

[2] *Textile World,* **71**, 2557 (1927).
[3] *Textile World,* **71**, 3071 (1927).

There has been a trend on the part of knitters to favor fine filament yarns for the better class of garments. In spite of their higher price, these yarns are in great demand and rayon manufacturers are generally making changes in their numbers to increasingly finer filaments. The advantages of this type of thread lie principally in an increased softness or more desirable "feel" of the garment, and in improved strength and wearing qualities.

General Reviews. The first comprehensive American treatise on the rayon industry has recently been published by Avram.[4] This work constitutes a valuable compendium of economic and technical developments and contains an excellent literature and patent bibliography. Recently two American periodicals [5] covering commercial, chemical, and mechanical phases of the new industry, have been welcomed into existence by both the manufacturer and the consumer.

General reviews of the patent literature have been published by Mullin.[6] Bayer [7] has assembled patents bearing on the treatment and handling of viscose rayon after spinning and Schulke [8] has published a review of the patents on coagulating media for viscose. Jentgen [9] discusses general improvements in manufacture. The dyeing of rayon yarns is treated by Hall,[10] who suggests precautions to be observed when applying different classes of dyestuffs.

The part played by four noted pioneers in the early days of manufacture is presented in a series of articles by Bennett and Hard.[11]

Domestic production and foreign importation are covered by Woolf.[12] Among other articles of interest may be mentioned these by Hubener,[13] Sturtevant, [14] and Wilson.[15] Perl [16] describes an interesting venture of O. Kohorn and Company of Chemnitz and Vienna, in the form of a rayon experimental plant and training school.

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[4] The Rayon Industry, New York, Van Nostrand, 1927, 622 p.

[5] *Rayon*, Rayon Publishing Co., New York. *The Rayon Journal*, Textile Reporting Co., New York.

[6] *Textile Colorist*, **48**, 459, 739, 813 (1926).

[7] *Melliand's Textilberichte*, **8**, 82 (1927).

[8] *Textileber.*, **7**, 320, 326 (1926).

[9] *Kunstseide*, **8**, 295, 383 (1926).

[10] *Textile Colorist*, **48**, 534 (1926).

[11] *Silk J.*, **3**, no. 25, 59; no. 26, 64; no. 27, 62; no. 28, 59, 64 (1926).

[12] *Textile World*, **70**, 1996 (1926).

[13] *Mon. Sci.*, **16**, 158, 249 (1926).

[14] *Textile World*, **71**, 319, 1198, 1741, 2643 (1927).

[15] *Ind. Eng. Chem.*, **18**, 829 (1926).

[16] *Textile World*, **70**, 2004 (1926).

Cellulose Researches. Although abstractly concerned with the physico-chemical properties of cellulose and its compounds, attention is directed to the admirable work of R. O. Herzog[17] as illustrating the type of research which is daily becoming of more importance to the rayon chemist. The determination of the size of crystallites in cellulose and its compounds has been achieved by means of X-ray spectrographs, with results in close agreement with values calculated from diffusion data. The swelling of cellulose by alkali hydroxides and other solutions has also been investigated by this method. Of particular interest is Herzog's theory of the ripening of viscose based on observations suggesting the formation of secondary colloidal particles from primary particles during ripening.

Although this work has been only in minor part concerned *directly* with artificial fibers or spinnable solutions, practically the entire field opened up by Herzog has such broad bearing on rayon processes and fundamental concepts that developments will be watched with keen interest.

In the field of new raw materials Richter,[18] of the Brown Company has developed an alpha fiber wood pulp containing 95% alpha cellulose. This pulp stands better than intermediate between ordinary pulp for rayon manufacture and the best cotton linters in respect to alpha content and constitutes an interesting high grade cellulose for rayon manufacture.

Viscose Process. Since about three fourths of the world's output of rayon is now manufactured by this process, chemical developments in this field find wide interest.

A general discussion of cellulose xanthate formation and viscose ripening has been given by Blanco.[18a]

Coagulating Baths. Supplementing an already voluminous patent literature covering coagulating media for viscose, a number of new compositions have been proposed. Mendel[18b] has developed a series of acid baths containing the phosphate ion. The advantages of these baths appear in spinning fine filaments and in their effect in minimizing sulfur deposition in the threads. A two stage precipitation for fine filaments is effected by means of sodium acid sulfite and ammonium chloride in the first bath and sulfuric acid with a soluble phosphate in the second bath.[19]

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[17] *Kolloid Z.*, 39, 252 (1926). *J. Phys. Chem.*, 30, 457 (1926). *Pulp Paper Mag. Can.*, 24, 694, 699 (1926). *Trans. Am. Electrochem. Soc.*, 51, Preprint (1927). *Papierfabr.*, 24, *Festheft.*, 94 (1926).

[18] U. S. P. 1,599,489 (Sept. 14, 1926); 1,602,553 (Oct. 12, 1926).

[18a] *Ind. Eng. Chem.*, 18, 1257 (1927).

[18b] U. S. P. 1,576,529; 1,576,530; 1,576,531 (Mar. 16, 1926); 1,580,844 (Apr. 13, 1926); 1,614,431 (Jan. 11, 1927).

Zinc, a well known coagulent, in concentrations of 1% to 3%, is now used by Dreaper [20] in concentrations between 4% and 10% in conjunction with known salts and acids for fine filament spinning. Dyeing qualities of the finished yarn are improved by van der Want and Bouman [21] by the use of small quantities of nickel or cobalt in the bath. The evolution of hydrogen sulfide during spinning is minimized by Hartogs [22] by the incorporation of ferric salts in ordinary acid baths. A new combination of sodium and ammonium sulfates with sulfuric acid is proposed by Dreaper.[23]

The spinning of unripe viscose from unripened alkali cellulose is accomplished by Kämpf,[24] through the use of either a low bath temperature (5°C.) or the addition to the bath of about 5% of the sulfonic acid of the condensation product from the action of phenol on finely ground sawdust or other substances rich in cellulose.

Crystallization of salts subsequent to spinning is avoided by Niederhauser and Sunderland [25] by adding to the bath about 2% of a soluble colloid, such as glue. Improvements in strength of the thread are claimed for the use of these constituents.

Cellulose Acetate Process. The bulk of investigation in this field concerns the application of dyes and methods or solutions for spinning. Mullen [26] has compiled an author, subject and patent index covering this process. New dyes and their method of application have been discussed by Baddiley and Hill,[27] Metzger,[28] Duisberg and Hentrich,[29] Ellis,[30] Hoz and co-workers,[31] Baddiley and co-workers,[32] and Rabe.[33]

Control of cross sectional shape is effected by Lahouse,[34] by spinning into a warm atmosphere partially saturated with the cellulose acetate solvent.

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[19] U. S. P. 1,580,843 (Apr. 13, 1926).
[20] U. S. P. 1,626,454 (Apr. 26, 1927).
[21] U. S. P. 1,596,906 (Aug. 24, 1926).
[22] U. S. P. 1,573,062 (Feb. 16, 1926).
[23] U. S. P. 1,583,534 (May 4, 1926).
[24] U. S. P. 1,575,210 (Mar. 2, 1926); 1,614,036 (Jan. 11, 1927).
[25] U. S. P. 1,625,562 (Apr. 19, 1927).
[26] *Am. Dyestuffs Rep.*, 15, 285 (1926)
[27] U. S. P. 1,611,986 (Dec. 28, 1926).
[28] U. S. P. 1,602,695 (Oct. 12, 1926); 1,610,961 (Dec. 14, 1926).
[29] U. S. P. 1,587,708 (June 8, 1926).
[30] U. S. P. 1,600,277 (Sept. 21, 1926); 1,618,413; 1,618,414; 1,618,415 (Feb. 22, 1927).
[31] U. S. P. 1,613,228 (Jan. 4, 1927).
[32] U. S. P. 1,616,103 (Feb. 1, 1927).
[33] U. S. P. 1,622,122 (Mar. 22, 1927).
[34] U. S. P. 1,583,475 (May 4, 1926).

For the wet spinning of acetate solutions Hübert, Leuchs and Lock [35] use a solvent composed of acetone and pyridine and a bath of strong calcium chloride solution. Hegan [36] precipitates an acetone solution of the acetate in a bath of oleic acid.

The acetylation of cellulose is catalyzed by Webb and Malm [37] by the additions of red phosphorus and chlorine into the reaction mixture of acetic acid and acetic anhydride at 60-65°C. Zadnowich [38] prepared a suitable solution of the acetate for spinning directly, by introducing chlorine into the acetylating mixture and later treating the chlorinated material with sulfur dioxide. Acetate solutions are stabilized by Mork [39] by the addition of about 2% of an organic salt of an alkali metal such as alkali oleates, acetates, etc. Further improvements in spinning have been proposed by Girardet,[40] Grillet,[41] and Dreyfus.[42] A method for the recovery of acetic acid is described by Bader.[43]

Particularly interesting is the novel reaction described by Nightingale [44] for the preparation of cellulose acetate. Cellulose in the presence of a neutral liquid, such as ether or benzene, is caused to react with ketenes to form cellulose acetate directly. Catalysts, such as zinc chloride, aid the reaction.

Nitrocellulose and Cuprammonium Process. The wet spinning of nitrocellulose is carried out by Bindschedler and Juer [45] in an alcoholic bath containing one or more soluble metal chlorides, in particular, zinc chloride. Roy [46] has designed a spinning cell suitable for evaporation and recovery of the solvent in dry spinning. The viscosity characteristics of nitrocellulose spinning solutions are controlled by Olsen and Aaronson [47] by pre-treatment of the cellulose with 5-10% sulfuric or hydrochloric acids at a temperature of 40-60°C.

Stretch spinning has always been favored in the cuprammonium process and Schubert [48] has proposed another method for drawing out the threads from the spinning nozzle. Elsaesser and Hartmann[49] describe a bath flow first counter current to the thread and later concurrent, for stretch spinning precipitation.

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[35] U. S. P. 1,583,717 (May 4, 1926).
[36] U. S. P. 1,599,233 (Sept. 7, 1926).
[37] U. S. P. 1,591,590 (July 6, 1926).
[38] U. S. P. 1,600,159 (Sept. 14, 1926).
[39] U. S. P. 1,607,474 (Nov. 16, 1926).
[40] U. S. P. 1,586,552 (June 1, 1926).
[41] U. S. P. 1,571,474 (Feb. 2, 1926).
[42] U. S. P. 1,620,636 (Mar. 15, 1927).
[43] U. S. P. 1,609,393 (Dec. 7, 1926).
[44] U. S. P. 1,604,472 (Oct. 26, 1926).
[45] U. S. P. 1,584,005 (May 11, 1926).
[46] U. S. P. 1,592,006 (July 13, 1926).
[47] U. S. P. 1,615,343 (Jan. 25, 1927).
[48] U. S. P. 1,619,768 (Mar. 1, 1927).

In the main, recent developments in connection with these two processes have covered mechanical, rather than chemical features.

Recent New Products. *Hollow Filaments.* The production of hollow filament of "blown rayon" is receiving attention abroad. The product possesses greater warmth, softness, and covering power than do ordinary yarns.[50]

An interesting application of electrolysis is used by Leuchs,[51] who electrolyzes a viscose solution forming minute air bubbles of a controlled size which remain in the filaments during coagulation and thus serve to impart to them their hollow structure.

Artificial Staple Fiber. Artificial staple fiber from viscose has been produced in Germany since the period of the war, and is now being imported in moderate quantities. The "spun rayon" yarn produced by spinning this staple after the manner of cotton spinning, has aroused considerable interest in the textile trade and although not yet an article of commercial domestic production, its development in this country seems imminent.[52]

"Immunized" Yarns. Zimmerman[53] has perfected a process for "immunizing" cellulose fibers, including rayon, to direct dyestuffs, but reactive to basic or cellulose acetate dyes. The process depends upon the action of *p*-toluenesulfonyl chloride on the mildly alkalized fibers and probably results in a new ester of cellulose, although this has not been isolated. Such yarns find use in cross dyeing or in the production of pattern effects.

Imitation Pongee. Threads resembling wild silk for use in imitation pongee are described by Rosenthal[54] in a process for coating silk or rayon irregularly with viscose and regenerating.

Cellulose Ethers for Spinning. These compounds were originally proposed as materials suitable for spinning by Lilienfeld, who is still active in this field. Possessing dyeing and soluble properties similar to those of cellulose acetate, but being superior in resistance to acids and alkalis, they are being widely investigated but are not yet to a commercial stage of manufacture in thread form.

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[49] U. S. P. 1,596,086 (Aug. 17, 1926).
[50] *Silk J.*, **2**, No. 19 (1925).
[51] U. S. P. 1,611,354 (Dec. 21, 1926).
[52] Canning, *Textile World*, 70, 2001 (1926); *Textile World*, 70, 2912 (1926); Cox, *Textile World*, 69, 3967 (1926); U. S. P. 1,627,037 (May 3, 1927).
[53] *Calico Printer*, 56, 184 (1926). U. S. P. 1,523,742 (Jan. 20, 1925).
[54] U. S. P. 1,617,544 (Feb. 15, 1927).

Altwegg and Maillard [55] purify crude solutions of the cellulose ethers by treatment with hydrochloric acid followed by aqueous precipitation. Hegan [56] uses as a spinning bath a mixture of a fatty acid and castor oil. Glover [57] precipitates the threads in a bath of a saponifiable oil alone. Lilienfeld [58] prepares a solution suitable for spinning in a mixture of nitromethane and a lower monohydroxy aliphatic alcohol. A novel spinning solution for cellulose ethers is described by Chauvissieu [59] who dissolves these bodies in ammonium thiocyanate solution.

Van Weyenbergh [60] describes an alkali cellulose especially adapted to etherification. New processes for the dyeing of cellulose ether rayon have been proposed by Eichwede and Fischer,[61] by Duisberg, and Hentrich, Weinand and Zeh,[62] and others.

Delustered Yarn. Delustered or partially delustered yarns are preferred by certain hosiery manufacturers. Bruckhaus [63] describes the delustering of rayon by precipitation of barium sulfate, aluminum soaps or tin phosphate on the finished yarn analogous to the weighing of natural silk. A somewhat similar effect is obtained by Dreaper [64] in a process applied before initial drying of the spun rayon.

Miscellaneous Rayon Treatments. Large quantities of caustic soda from initial mercerization in the viscose process are usually sent to waste. Griffin [65] has devised a scheme for dialysis on a large scale whereby this liquor may be separated from colloidal impurities and recovered for use.

Improved washing of rayon in the "cake" form is effected by Kämpf [66] by first submitting the fibrous mass to a partial vacuum for the removal of by-product carbon bisulfide after which washing proceeds with cold water.

Treatment of fibers of regenerated cellulose with formaldehyde and hardening agents has long been known under the term of "stenothage." [67] This process actually effects a considerable increase in wet strength but causes brittleness and difficulty in dyeing. Recently, however, Karplus[68] has proposed modifications in the method which it is claimed eliminates the undesirable features of previous treatments. It is probable that a new compound is formed through condensation of the OH groups of the cellulose with formaldehyde.

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[55] U. S. P. 1,599,508 (Sept. 14, 1926).
[56] U. S. P. 1,599,233 (Sept. 7, 1926).
[57] U. S. P. 1,599,230 (Sept. 7, 1926).
[58] U. S. P. 1,599,569 (Sept. 14, 1926).
[59] U. S. P. 1,622,368 (Mar. 29, 1927).
[60] U. S. P. 1,569,692 (Jan. 12, 1926).
[61] U. S. P. 1,599,748 (Sept. 14, 1926).
[62] U. S. P. 1,587,708 (June 8, 1926).
[63] *Rayon J.*, 1, no. 4, 21, 26 (1926).
[64] U. S. P. 1,604,889 (Oct. 26, 1926).
[65] U. S. P. 1,573,703 (Feb. 16, 1926).
[66] U. S. P. 1,579,711 (April 6, 1926).
[67] U. S. P. 995, 852 (June 20, 1911).

Cross[69] presents a method for preventing or controlling the shrinkage of the spun rayon thread during drying.

Films of Regenerated Cellulose. The commercial production of regenerated cellulose in transparent sheet form has been established in this country by the Brandenberger[70] process, and since its production from viscose is chemically so closely allied to the rayon process, it has been considered within the scope of this chapter to cite recent developments in this field.

Pfund,[71] of Johns Hopkins, finds that this material, commercially known as cellophane, possesses a remarkable transparency to ultraviolet light in the range of 2400-3400 A.U. and suggests its use in windows for heliotherapy. It not only possesses greater transparency than do esters and ethers of cellulose, but has been found to exhibit a minimum of yellowing with age. Pfund further points out that it possesses the property of double refraction, both wet and dry, and since it is procurable in large sheets, it may be used for the production of quarter and half wave plates of large area. The high impermeability of this material to gases as well as its properties as a dialyzing membrane has introduced it into a variety of new and unexpected uses in scientific laboratories.

An interesting process in this field is the recent production of cellulose sausage casings from viscose as worked out by Henderson and Dietrich.[72] Bottle caps and other nearly hollow bodies are produced from viscose by the process of Czapek.[73]

Feith and Ziegler[74] have described a process for a transparent sheet material from cuprammonium cellulose solutions. Taylor[75] produces this material by electrical deposition of cellulose from its solution in cuprammonium hydroxide or zinc chloride on to a moving belt from which it is later stripped off. The principle of precipitation and regeneration of viscose by acids on a moving belt or wheel is also the basis of a patent to Czapek,[76] who states that viscose may be so manipulated.

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[68] U. S. P. 1,591,922 (July 6, 1926).

[69] U. S. P. 1,611,001 (Dec. 14, 1926).

[70] U. S. P. 1,601,289 (Sept. 28, 1926).

[71] *Bull. Johns Hopkins Hospital,* 40, no. 4, 228 (1927).

[72] *Ind. Eng. Chem.,* 18, 1190 (1926); U. S. P. 1,616,971 (Feb. 8, 1927); 1,601,686 (Sept. 28, 1926).

[73] U. S. P. 1,591,000 (June 29, 1926).

[74] U. S. P. 1,611,175 (Dec. 21, 1926).

[75] U. S. P. 1,590,601; 1,590,602; 1,590,603 (June 29, 1926).

PROBLEMS

In suggesting the list of research topics below an attempt has been made to propose subjects upon which it should be possible to complete an investigation in approximately a year and which might profitably be pursued without costly equipment other than that already available in many of our larger universities. Of necessity a large share of investigational work must and can be adequately carried out only by manufacturers, but no reference is implied in the following list to this type of research.

1. A number of interesting relationships between the cuprammonium viscosity of various types of wood pulp and cotton linters, and the viscose viscosity of these materials await investigation. Relationship curves between these two viscosities for alkali cellulose aged at various temperatures and for varying periods of time are needed.
2. Further work is needed in standardizing the alpha cellulose determination especially as applied to regenerated cellulose (films and fibers). The usual methods often become inconsistent when applied to regenerated cellulose.
3. Chemical and physical changes incident to the ripening of viscose have been studied, but this still remains a very fruitful field for further investigation by the pure research chemist.
4. Chemical and physical changes incident to the aging of alkali cellulose, need further study including the important role of oxygen during aging. Its rate of absorption of oxygen, the products formed, and the dependence of these factors on the composition of and impurities (catalysts) in alkalized cellulose have many practical as well as theoretical bearings.
5. Isolation and identification of the reaction products of alkalized cellulose and aryl sulfonyl chlorides.
6. A study of the fine structure of regenerated cellulose by the ultramicroscope in plain and polarized light as well as that of chemical transformation products and swollen cellulose.
7. Isolation and identification of the reaction products of regenerated cellulose and formaldehyde.
8. A large poundage of rayon waste consisting of a highly purified form of cellulose is annually produced. This product is chemically a very reactive form of cellulose and is awaiting development of a use in chemical manufacture where its purity and reactivity may be exploited.
9. A study of solutions of cellulose in calcium thiocyanate, the degree of degradation, hydration and dispersion with various conditions of solution, means of regenerating the cellulose from these solutions and properties of the resultant films or threads.
10. A further study of the xanthation reaction is needed under very carefully controlled conditions with respect to products formed, temperatures, pressures, presence of air or inert gases and degree of swelling of the mercerized cellulose.

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[76] U. S. P. 1,590,999 (June 29, 1926).

Chapter XLIV.

Explosives.

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Among the historical surveys of the explosives industry which have appeared during the past year, mention may be made of that by Reese, "Twenty-five years' progress in high explosives," [1] which period covers the history of the Eastern Laboratory of E. I. du Pont de Nemours & Co. A longer range but less detailed review of the development of the explosives industry in the United States appeared in the Golden Jubilee number of the Journal of the American Chemical Society under the title "A half century of industrial chemistry in America, 1876-1926," by Munroe.[2] Davis [3] discusses Kunckel's discovery of mercury fulminate and places the date of the discovery prior to 1703, or more than a hundred years before Howard's announcement.

As is now well known, industrial dusts constitute a special hazard for, if in the least combustible, they may form explosive mixtures with air or other supporters of combustion. Dust explosions are made the subject of special investigation in the Bureau of Chemistry, Department of Agriculture, by Price and his associates. Among his recent publications are "Some chemical and engineering aspects of dust explosions" and "The other side of dust explosion prevention" issued in mimeographed form by the Bureau; "A recently developed dust explosion and fire hazard," [4] written in collaboration with Brown, and "Dust explosion hazards: Sugar and cocoa, pulverized fuel systems and starch factories," [5] a committee report for discussion of codes. Finally there is to be noted "Safety codes for the prevention of dust explosions" issued by the U. S. Bureau of Labor Statistics as Bulletin No. 433 (1927).

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[1] *Chem. Met. Eng.*, 34, 251 (1927).
[2] *J. Am. Chem. Soc.*, 48, no. 8a, 203 (1926).
[3] *Army Ordnance*, 7, 62 (1926).
[4] U. S. Dept. of Agr., Dept. Circular 171 (1921).
[5] Preprint, Nat. Fire Protection Assoc., 21 p., 1927.

Among observations on dust investigations is recorded that of Allison and Bauer on the "Explosibility of oil shale dust,"[6] who find this dust to be inflammable and to form explosive mixtures with the air to such a degree that, since in mining and handling the formation of dust is unavoidable, the same precautions should be taken with it as with coal.

An unexpected dust explosion occurred at Baltimore, January 4, 1927, during the loading of the French barque Richelieu[7] with water gas tar residuum. Tar has long been loaded on shipboard in the manner then followed and this is said to be the first dust explosion on shipboard recorded. It is understood this residuum was the product of a new process.

There are other effects of dust that are proper subjects for consideration in connection with explosives and explosions as illustrated in "Effects of coal dust on the gases resulting from detonating permissible explosives" by Crawshaw and Jones.[8] Coal dust is produced in the drilling of boreholes in coal and some of it may remain in the hole so that, as the explosive is charged into the borehole, this coal dust may accumulate behind, around or in front of the charge, or some may occupy each of these positions. Moreover it is not an uncommon practice in mines to stem the charge with these drillings, known as "bug dust." Permissible explosives are compounded to produce definite amounts of predetermined gaseous products when exploded confined in clean boreholes. Crawshaw and Jones have sought to ascertain, by means of the "dumb-bell," the effect of this coal dust in the borehole on the explosive system, and they conclude that when a shot does the normal amount of work, coal dust in the drill hole will react to only a negligible extent and will not appreciably increase the volume of noxious gases evolved by the explosion. When, however, a blownout shot occurs, the coal dust in front of the explosive may be ignited by the flame from the hot combustible gases liberated on detonation. This may readily occur on contact with the air. As a result, a large quantity of poisonous gases may be produced or a coal dust explosion be initiated that may propagate over a large part of the mine. Both these dangers may be guarded against by thoroughly cleaning the drill holes before loading, and by the use of sufficient non-combustible stemming.

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[6] Bureau of Mines, Repts. of Investigations No. 2758 (1926).
[7] *Quarterly Nat. Fire Protection Assoc.*, **20**, 382-384 (1927).
[8] *Coal Age*, **30**, 906 (1926).

In the chapter on Explosives, in volume 1, attention was called to the menace from poisonous gases in the products of the combustion or explosion of explosives, and especially to the review of the subject by Walton.[9] The results of the experimental work carried out at Edgewood Arsenal appeared under the title "Deflagration products of smokeless powder: An analytical and physiological study" by Knight and Walton.[10] As much as 9.4% of NO_2 and 33.3% by volume of CO were found in samples taken 25 seconds after firing. The physiological effect from exposure came not only from these substances but also from the CO_2 and the high temperature existing which compelled more rapid breathing, while the high temperature also increased the activity of the gases. The "nitrous gases" produced pulmonary edema which developed later than the CO poisoning effect.

There are other circumstances when poisoning may result from burning explosives as in the destruction by fire of the boxes in which explosives have been packed, and packing, lining paper and wrappers from the cartridges, for these often have attached or absorbed nitroglycerin and other components of explosives. Our attention has recently been called to poisoning resulting from burning such "trash" within a mine between shifts. Of course, carbon monoxide, methane and other gases which would form explosive mixtures may also be produced.

The behavior of mixtures of combustible gas or vapors with air or oxygen, and sometimes with inert gases admixed, has continued the favorite subject of study by many. In the study of "The explosibility of methane and natural gas" by Coward, Jones, Dunkle and Hess,[11] mixtures of natural gas with air were compared with mixtures of methane and air as to relative ignitibility, inflammability limits, and speed of propagation of flame. Natural gas is ignited at a somewhat lower temperature than methane but at a much higher one than ethane. The ignition temperature of a sample of Pittsburgh natural gas was almost constant over the whole range of inflammable mixtures with air while that of methane increases and that of ethane decreases with the concentration. The time lag on ignition was markedly less for natural gas than for methane. Both lower and upper limits of inflammability are somewhat less for natural gas than for methane. The lower limit can be calculated fairly accurately and the upper approximately from the limits of the individual hydrocarbons and composition of the natural gas. The lower limit can be obtained with equal accuracy (but not the upper) from a curve and a combustion analysis which gives merely the ratio between the contraction on explosion and the volume of carbon dioxide formed thereby. The limits of pure hydrocarbons for upward inflammability, determined in apparatus of size such that the results apply to industrial conditions, are: methane, 5.24-14.02; ethane, 3.22-12.45; propane, 2.37-9.5; butane, 1.86-8.41. The speed of flame in certain natural gas-air mixtures may be slightly higher than in any methane + air mixture. The speeds of uniform movement of flame in any natural gas + air mixture can be calculated from the analysis of the gas and the known flame speeds in mixtures of the individual hydrocarbons and air. These observations were made in a tube but 1 in. in diameter. It remains to be seen if similar conclusions hold for large-scale inflammation. The behavior of flame during the vibratory phase is similar for a typical natural gas and methane. These general conclusions show that natural gas is somewhat more inflammable than methane. Therefore, the use of natural gas, rather than methane, for testing electrical equipment, flame safety lamps, and explosives for their safe use underground is justified so far, for any difference between natural gas and methane is on the safe side; and, moreover, the differences are not so great that any hardship is imposed on the makers of such equipment by the slightly greater stringency of the tests with natural gas.

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[9] "A Survey of American Chemistry," 1, 237 (1927).

[10] *Ind. Eng. Chem.*, 18, 287 (1926).

[11] Mining and Metallurgical Investigations, Carnegie Inst. Tech. and U. S. Bur. of Mines, Bull. 30 (1926).

Coward and Jones[12] have also studied the "Mechanism of the uniform movement in the propagation of flame." In this investigation the speed of uniform movement of flame in mixtures of methane with air and with artificial atmosphere, composed of 20.9% oxygen and 79.1% argon or helium, has been observed in tubes of various diameters for upward, downward and horizontal propagation of flame with results indicating that the important factors determining flame speed are (1) the heat developed in the flame and the heat capacities of the burnt and unburnt mixtures, (2) the rate of chemical reaction. The rate of transmission of energy from the flame, whether by conduction of heat or some form of readily absorbed radiant energy, is so rapid that but little change in flame speed is observed when helium (of high thermal conductivity and low absorption for radiant energy) is replaced by argon (of low thermal conductivity and higher absorption for radiant energy), the inert gas being present to the extent of about three-fourths of the whole mixture. It is suggested that the temperature coefficient of the rate of oxidation of methane is relatively small at flame temperature.

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[12] *J. Am. Chem. Soc.*, **49**, 386 (1927).

The behavior of vapor mixtures has a special interest because of their use in internal combustion engines. Among investigators in this field are Brown and Watkins,[13] who report that the data obtained indicate that the rise of pressure in a progressive homogeneous reaction increases with molecular weight in the paraffin series; varies inversely with the number of methyl groups added in the benzene ring in the benzene series; is approximately the same for normal octane and benzene, normal heptane and toluene, and for normal hexane and xylene; is about the same for higher alcohols as for corresponding paraffin hydrocarbons; and is exceedingly rapid for ethyl ether. When the data of this paper are interpreted with the accepted fact in mind that the aromatic hydrocarbons do not produce "knocks" so readily as paraffin hydrocarbons, it becomes evident that the rate of rise of pressure in a progressive homogeneous explosion cannot be the sole factor determining *the tendency of a fuel to knock in an internal-combustion engine.*

The behavior of liquid fuels whose vapors are employed in the production of explosive mixtures for use in motors has also engaged the attention of Rosecrans,[14] who says that the changes in the composition of liquid fuels for internal combustion engines and the tendency towards the use of higher compression ratios, which frequently result in "fuel knock," indicate the desirability of a more detailed and complete knowledge of the actual mechanism of explosive reactions. The object of this investigation was a study of the flame propagation in a closed cylindrical bomb and a comparison of results of a theoretical analysis of flame propagation with the actual phenomena as observed by means of photographic records, while incidentally observing "flame arrest" and other obscure processes of explosive reactions reported by others. This investigation was limited to the study of the explosion of mixtures of ethyl ether and air in a cylindrical bomb of constant volume, two such bombs of the same diameters but different lengths being used. The theoretical discussion, after the method of Nagel, the description of the apparatus used, and the methods of experimentation followed are set forth quite fully with many illustrations, graphs and tables, and the conclusions are that the results of the theoretical analysis conformed approximately to the experimental ones obtained by photographing the flame propagation. The theoretical flame propagation curves generally differed from the experimental ones by amounts which can be accounted for by the heat loss which occurs in the latter. The experimental results, on the whole, confirm those of Woodbury, Lewis and Canby in that as a rule, but apparently not always, the flame fills the bomb at the time that maximum pressure is attained. The experimental results do not furnish any evidence of the dependence of the velocity of flame propagation on the initial temperature. The flame arrest phenomena appear in all the flame photographs, occurring quite uniformly at about one-half the length of the bomb from the igniting point. At the time of the flame arrest the pressure had, in general, risen to about 25% of its maximum. The hypothesis of the flame arrest being caused by spherical pressure waves, or such waves reflected from the walls of the bomb was disproved as was that the flame arrest was caused by a sound wave reflected from that end of the tube opposite the igniting point. The hypothesis that the flame arrest is due to the great decrease in density of the gases within and behind the flame front causing a momentary extinction of the flame does not conflict with any known facts regarding the flame front. From the characteristics of the explosion and compression of the burned and unburned gases during an explosion the existence of afterburning and adjustment of chemical equilibrium behind the flame front was demonstrated. The relative proportion of the total flame velocity due to chemical reaction velocity, for the mixtures investigated, varied from 15 to 85% during the progress of the explosion. The results indicate that the reaction velocity is a function of the pressure and an equation suggesting this relation has been indicated.

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[13] *Ind. Eng. Chem.*, 19, 280 (1927).
[14] Univ. of Ill., Eng. Expt. Station, Bull. No. 157 (1926).

Perrott[15] has investigated the "Factors in the ignition of methane and coal dust by explosives," finding that an air-space between the explosive and stemming reduces the safety somewhat. The conditions of greatest relative safety are loading the explosive tight in the borehole and tamping it with either a distinctly moist inert stemming such as damp fireclay or a finely pulverized stemming such as rock dust. The use of coal dust as stemming increases the likelihood of the ignition of gas or dust from a blown-out shot. The explosive gas mixture most sensitive to ignition by permissible explosives contains from 7.5 to 8% of natural gas. On either side of the limits, 7 to 8.5, the sensitiveness diminishes rapidly. A balanced explosive is most likely to cause an explosion of a 7 to 8.5% mixture but an under-oxidized explosive is more likely to cause ignition of gas mixtures near the lower limit and this is the condition most commonly met with in practice. Definite indications were obtained that that explosive having the higher rate of detonation is the more likely to ignite a gas + air mixture. Photographs of flames from explosives fired in air serve to divide explosives into groups as regards safety, and, taken in connection with the composition of the explosive and its rate of detonation, promise to throw light on the mechanism of ignition.

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[15] *Am. Inst. Mining Met. Eng.*, Preprint No. 1604-F (1926).

There is yet much to be learned regarding explosive phenomena. They are so rapid as to escape visual observation but much may be learned through modern methods of photography which can record separate events. In "Photographic measurement of rate of detonation of explosives" Perrott and Gawthrop[16] describe a photographic apparatus they have devised through the stenopaic lens of which the image of a file of explosive undergoing detonation can be taken on a moving film, the image being produced by the light emitted by the explosive. From a knowledge of the rate at which the film was moving and the degree of inclination of the image from the vertical the rate at which detonation proceeded through the file of explosives was calculated. Determinations were made of four different permissible explosives, a 40% nitroglycerin dynamite, and a 40% ammonia dynamite, and the results obtained compared very well with those obtained in determinations on the same explosives by means of the Mettegang recorder. Incidentally it was shown that when the detonation of a permissible explosive of ammonium nitrate-nitroglycerin type is initiated by an explosive detonating at a much higher rate, the characteristic rate of the permissible is unchanged. Also that some types of permissibles are flameless when detonated in the open.

These same investigators[17] have applied their photographic method to the study of the "Propagation of detonation across an air-gap between two cartridges of explosive." Files of a variety of detonating explosives, both in continuous and in discontinuous files, were detonated and the rates of detonation determined by means of the Mettegang recorder, and by a photographic method. In the discontinuous files, usually a single air-gap, varying in the different experiments from 1.5 to 48 inches, intervened between the part of the charge in which the detonation was initiated and the second part in which it was effected by "influence"; but in one set of experiments a file was used in which a 3 inch air-gap was repeated four times. The conclusions drawn from the experiments with the Mettegang recorder were (1) for explosives of low rate of detonation, 1700 m./sec., the velocity of propagation across an air-gap betwen two cartridges is at first considerably higher than the rate of detonation of the explosive, but falls off regularly until the second cartridge fails to detonate. (2) With explosives of a rate about 3000 m./sec. the velocity across the air-gap is about equal to that of the explosive over an interval of 4.5 to 7.5 inches from the end of the initiating cartridge. It then falls off regularly until the second cartridge fails to detonate. (3) For explosives of high rate, 4800 m./sec., the velocity in the air-gap is equal to that of the explosive for about 1.5 inches, then it falls off linearly until a gap of 27 inches is reached, after which the rate of decrease of velocity is less rapid until, at a gap of 48 inches, the second cartridge does not always detonate. The velocity over the interval 42 to 48 inches is about 730 m./sec. (4) Explosives containing ethylene glycol dinitrate propagate across a greater air-gap and maintain a higher average velocity across the air-gap than similar explosives containing nitropolyglycerin do. This is particularly evident in explosives with low rates of detonation. Photographic observations on a moving film in general confirmed the above. When instead of wrapping the file in Manila paper it was enclosed in glass tubes, under the superior confinement, the speed in the air-gap is considerably greater than the rate of detonation of the explosive, and is maintained for a greater distance while a luminescence is propagated through the air which seems coincident with the disturbance responsible for detonating the second cartridge. Laffitte holds that the pressure wave or shock wave sent out from the explosive, by compression, raises the temperature of the air until it becomes luminous. Perrott and Gawthrop from their observations take issue with this, rather believing the luminescence due to reactions in the gases projected from the explosive.

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[16] *J. Franklin Inst.*, 203, 103 (1927).
[17] *J. Franklin Inst.*, 203, 387 (1927).

"The detonation wave from solid explosives" has also been investigated by Holmes.[18] Using the modified Dautriche method in the study of the sensitiveness of explosives to explosion by influence Holmes has confirmed the observations of Comey and Laffitte that, while in general there is a tendency for the rate of detonation attained within the explosives file to diminish as the explosion products leave the file, there are explosives in which the rate is greater in the products beyond the file than within the explosive itself, and he finds the latter among detonating explosives having the lower rates of about 2000 to 2500 meters per second. This increase may attain in the space beyond the file from 100 to 300 meters per second greater than within the file, while with explosives having an internal rate of 5000-6000 meters per second the immediate exterior may decrease around 4400 meters. Most observations were made with cartridges as in the air-gap test but some with spheres of the explosive, measurements showing the existence of a zone of uniform movement beyond the explosive, depending on the diameter of the cartridge or the sphere. With a 1.25 inch cartridge this zone extended 10 inches. With a sphere 4 inches in diameter it extended 25 inches. Holmes finds an explanation for this behavior in either the velocity of sound at the prevailing temperature or, preferably, in the kinetic velocity of the gaseous particles, the latter implying the existence of momentary temperatures of over 40,000°C at the wave front. Such extremely high temperatures are held to be due partly to the heat of combustion of the ingredients of the explosive but more to the enormous pressures developed at the moment of explosion, adiabatic conditions being assumed in the calculations.

The introduction of ethylene glycol dinitrate in partial substitution for nitroglycerin in dynamites has led to a study of this glycol and its derivatives at the Bureau of Mines Experiment Station resulting in the publication of "Ethylene glycol: An evaluation of available information on the physical properties of this compound" by C. A. Taylor and Wm. H. Rinkenbach[19] and "The properties of glycol dinitrate," "The properties of diëthylene glycol . . ." and "Glycol dinitrate in dynamite manufacture, . . ." all by Rinkenbach.[20]

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[18] *J. Franklin Inst.*, **203**, 549 (1927).
[19] *Ind. Eng. Chem.*, **18**, 676 (1926).

The results of the firing tests, at the Explosives Experiment Station at Bruceton, Pa., of explosives containing ethylene glycol dinitrate have been such as to warrant explosives containing it, in part substitution for nitroglycerin, being carried on the Permissible List. Discrediting statements from German sources as to the practicability and feasibility of this substitution are met by the above publications and "Commercial production of ethylene glycol" by Weidlein.[21]

A publication of general interest, the title of which explains itself, is "Electric shot-firing in mines, quarries and tunnels," by Ilsley and Hooker,[22] which presents an extended review of the development of the methods and devices and is profusely illustrated with forms of initiating devices, firing mechanisms and layouts for the wiring.

Although the title, "Thermit and icebergs," of an article by Barnes,[23] offers no suggestion of explosives, there will be found some most vivid pictures of explosions of ice masses due, it is believed, to the explosion of mixtures of the air with hydrogen resulting from the reduction of water by the thermit. On page 614 is an account of the action of thermit on solid CO_2 where, in one instance, an explosion occurred. The complete reduction of CO_2 to C by the burning metal has a special significance to the explosives chemist.

As suggestions for research there may be mentioned the determination of the depression of the freezing points of nitroglycerin, nitroglycol and other liquid explosive compounds by various nitrocompounds and nitrates, especially nitric esters, dissolved in them.

Also the determination of the explosive limits of commonly used vaporous combustible liquids or gases in admixture with air. An example is found in formaldehyde which, in certain industries, has come to be used on a large scale, where it is alleged to have given rise to serious explosions.

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[20] *Ind. Eng. Chem.*, 18, 1195 (1926); *ibid.*, 19, 474 (1927); *Chem. Met. Eng.*, 34, 296 (1927).

[21] *Chemical Age*, 16, 442 (1927).

[22] Bureau of Mines, Bull. No. 240 (1926).

[23] *J. Franklin Inst.*, 203, 611 (1927).

Chapter XLV.

Azo Dyes and Intermediates.

Emmet F. Hitch,

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As stated in the survey for last year, "the progress in the chemistry and chemical technology of azo dyes and intermediates over any given period is shown by the amount of theoretical work done in this field as evidenced by publications of the results of such investigations, by the number of new colors placed on the market by the manufacturers, by the improvements in quality and dyeing properties of the old dyes, by economies in manufacturing operations as shown by price reductions, and by the number of patents issued in this field."

Some of our universities and colleges and the government laboratories are continuing to show an interest in azo dyes and intermediates. The Bureau of Standards has contributed an article entitled "Subsidiary Dyes in Commercial Agalma Black 10B" by Brode.[1] This describes spectrophotometric methods for the identification and quantitative estimation of these subsidiary dyes. Work has been continued on the reduction products of azo dyes by Holmes of the Color Laboratory of the Bureau of Standards. These articles are being published in The American Dyestuff Reporter. Berliner and May[2] of the Color Laboratory have made studies on the vapor pressure of the toluidines. The vapor pressures of the three isomeric toluidines were determined from 40°C. to a few degrees above their normal boiling points. The normal boiling points found were as follows:—*o*-toluidine 199.84°, *m*-toluidine 202.86°, *p*-toluidine 200.35°. Work has also been done at the same laboratory on the vapor pressure of α- and β-naphthol by May, Berliner, and Lynch.[3] The boiling points at atmospheric pressure were found to be 288.01° for α-naphthol and 294.85° for β-naphthol. Holmes and Berliner [4] have made a study of dye solution phenomena with variation in hydrogen ion concentration, with particular reference to dye identification. Heid [5] of the Color Laboratory has made an investigation of the rate of conversion of naphthalene-2,7-disulfonic acid to the isomeric 2,6-acid at 160° in the presence of sulfuric acid. It was found that as much as 42% of the 2,7-acid is converted to the 2,6-isomer before equilibrium is established. A method of purifying the 2,7-disulfonic acid is described. At the Hygienic Laboratory, U. S. Public Health Service, Gibbs [6] has investigated a new method of separating *p*-cresol from its isomers and studied its boiling point. The boiling point for *p*-cresol at 760 mm. pressure was found to be 202.32°C. Wheeler and his co-workers at the University of North Carolina have continued work on *p*-cymene and its derivatives. 2-Amino-6-nitro-*p*-cymene and certain new azo dyes have been prepared.[7] This intermediate is obtained by partial reduction of 2,6-dinitrocymene with ammonium sulfide. A number of monoazo dyes were prepared by diazotizing the aminonitrocymene and coupling with phenols, naphthols, and their sulfonic acids. The 2,6-diamino-*p*-cymene has also been prepared in the same laboratory.[8]

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[1] *Ind. Eng. Chem.*, **18**, 708 (1926).
[2] *J. Am. Chem. Soc.*, **49**, 1007 (1927).
[3] *J. Am. Chem. Soc.*, **49**, 1012 (1927).

As a measure of the progress that the industries have made in this field it is interesting to note that about forty-one new dyes have been announced by American manufacturers during this period. It is difficult to determine exactly how many of these new dyes represent new and original colors which are the result of investigation in the industrial research laboratories. It is estimated, however, that at least twelve of these colors are distinctly new chemical individuals. Some of these twelve colors represent a real advance in color making since they are superior to dyes of similar shade in fastness properties or in their suitability for use on various fibres. There is an increasing demand on the part of the public for faster colors. It is interesting to note that this demand is being gradually met by the azo dye producers. For example, it is not now necessary for the dyer to use vat colors to obtain the required fastness to light in some shades. A few of

[4] *Am. Dyestuff Reporter* **16**, 81 (1927).
[5] *J. Am. Chem. Soc.*, **49**, 844 (1927).
[6] *J. Am. Chem. Soc.*, **49**, 839 (1927).
[7] *J. Am. Chem. Soc.*, **49**, 494 (1927).
[8] *J. Am. Chem. Soc.*, **49**, 572 (1927).

the azo dyes placed on the market this year are as fast to light as vat colors of similar shade.

Eleven patents on azo dyes have been granted during this period to Americans. These patents represent the result of research work in this country.

U.S.P. 1,594,805 (Aug. 3, 1926, Henry Wenker, National Aniline & Chemical Co.), covers the azo dyes prepared by phosgenating amino azo compounds such as, for example, a mixture of *p*-aminobenzeneazo-3,6-disulfo-1-amino-8-naphtholazobenzene and *p*-aminobenzeneazosalicyclic acid or a mixture of one molecular equivalent of *p*-aminobenzeneazo-3,6-disulfo-1-amino-8-naphtholazo-(*p*)-aminobenzene and two molecular equivalent of *p*-aminobenzeneazosalicyclic acid. These compounds are direct dyes, giving green shades on cotton.

U.S.P. 1,594,828 (Aug. 3, 1926, L. W. Geller, National Aniline & Chemical Co.), covers the azo dyes prepared by phosgenating a mixture of amino azo compounds comprised of different or equimolecular proportions of 4-hydroxy-4′-aminoazobenzene-5-carboxylic acid and 4′-chloro-2-methyl-5-alkoxy-4-aminoazobenzene-5′-sulfonic acid. This mixture of compounds dyes unmordanted cotton yellow shades of good fastness to light and washing.

U.S.P. 1,605,973 (Nov. 9, 1926, J. B. Oesch, Newport Co.), covers triazo dyes prepared from acetyl amino-Cleve's acid, two molecular proportions of *m*-toluidine, and one molecular proportion of salicyclic acid or a halogen or alkyl derivative of salicyclic acid. These dyes give fast to light orange-brown shades on cotton.

U.S.P. 1,605,974 (Nov. 9, 1926, J. B. Oesch, Newport Co.), covers tetrakisazo dyes prepared from aminoazobenzene or toluene mono- or disulfonic acids, two molecular proportions of *m*-toluidine, and one molecular proportion of salicylic acid or a halogen or alkyl derivative of salicyclic acid. The dye from aminoazotoluenedisulfonic acid, two molecular proportions of *m*-toluidine and one of salicyclic acid gives yellowish-brown shades on cotton.

U.S.P. 1,609,793 (Dec. 7, 1926, to P. Caccia), covers a blue disazo dye suitable for dyeing artificial silk prepared by coupling benzidine tetrazo to a mixture of H-acid and 2-naphthylamine-5-sulfonic acid in the presence of a soluble cyanide.

U.S.P. 1,610,946 (Dec. 14, 1926, E. F. Hitch and F. H. Smith, E. I. duPont deNemours & Co.), covers polyazo dyes prepared from two molecular equivalents of benzidine, one molecular equivalent of H-acid, and one equivalent of another intermediate such as salicyclic acid, *m*-toluylenediamine, a naphtholsulfonic acid or an aminonaphtholsulfonic acid, then treating the compound thus formed with sodium bisulfite or with acid at the boiling temperature. These dyes give yellowish-green to blue to black shades on cotton and silk.

U.S.P. 1,615,550 (Jan. 25, 1927, J. B. Oesch, Newport Co.), covers trisazo dyes prepared from acetyl amino-Cleve's acid, two molecular proportions of *m*-toluidine and one molecular proportion of phenylmethylpyrazolone or its substitution products. The dye made from acetyl amino-Cleve's acid, two *m*-toluidines and 1,*p*-sulfo-phenyl-3-methyl-5-pyrazolone dyes cotton in orange-brown shades, very fast to light.

U.S.P. 1,615,551 (Jan. 25, 1927, J. B. Oesch, Newport Co.), covers tetrakisazo dyes similar to those described in Patent No. 1,615,550 except that acetyl amino-Cleve's is replaced by amino-azobenzene- or toluene-mono- or disulfonic acids. These compounds are yellowish-brown dyes for cotton.

U.S.P. 1,616,850 (Feb. 8, 1927, L. H. Fleet, National Aniline & Chemical Co.), covers trisazo or polyazo dyes from resorcinol. They are prepared by coupling three molecular proportions of the same or different diazotized aromatic amino compounds to one molecular proportion of resorcinol. At least one of the amino compounds contains a carboxyl or sulfonic acid group. The dye obtained by combining two moles of sulfanilic acid and one mole of xylidine to resorcinol is a brown dye suitable for leather, silk, and wool.

U.S.P. 1,617,244 (Feb. 8, 1927, R. J. Fletcher, Amalgamated Dyestuff & Chemical Works), covers the disazo dye from diamino-diphenylurea and chromotrope acid. This dye is prepared by coupling diazotized *p*-nitroaniline to chromotrope acid, reducing and phosgenating this azo compound. It is a direct violet dye having excellent fastness to light.

U.S.P. 1,618,762 (Feb. 22, 1927, T. H. Leaming, National Aniline & Chemical Co.), covers the process of producing the copper compound of the azo dye produced by combining two molecular equivalents of anthranilic acid to rhoduline acid (5,5′-dihydroxy-2,2′-dinaphthylamine-7,7′-disulfonic acid). This process consists in treating the disazo dye with a copper salt and caustic soda at about 85°C. for approximately one hour. The compound thus formed dyes cotton and silk reddish-violet shades.

Nine patents have been granted on intermediates for azo dyes.

These patents indicate the nature of the research work done by Americans in this field.

U.S.P. 1,591,688 (July 6, 1926, W. L. Spalding, National Aniline & Chemical Co.), covers a process for the production of benzidine flakes.

U.S.P. 1,594,390 (Aug. 3, 1926, N. E. Van Stone and C. E. Deeds, Sherwin-Williams Co.), covers a process for the manufacture of β-naphthol in the form of flakes.

U.S.P. 1,594,547 (Aug. 3, 1926, R. A. Nelson, National Aniline & Chemical Co.), covers a process for the production of α-nitronaphthalene-β-sulfonic acids, which may be used to produce Cleve's acids.

U.S.P. 1,595,299 (Aug. 10, 1926, W. J. Hale, Dow Chemical Co.), covers a method of preparing phenol by direct oxidation of benzene at high temperatures and pressures in the presence of caustic alkalies and the oxides of certain metals.

U.S.P. 1,607,618 (Nov. 23, 1926, W. J. Hale and E. C. Britton, Dow Chemical Co.), covers a process for the preparation of phenol and its homologues from halogenated benzene hydrocarbons. In this process the halogenated benzene compound is hydrolyzed by a solution of caustic alkali in the presence of diphenyl oxide.

U.S.P. 1,607,824 (Nov. 23, 1926, W. J. Hale and J. W. Britton, Dow Chemical Co.), covers a process for making aniline or other aryl amines from chlorobenzene or other halogenated aromatic hydrocarbons by the action of ammonia in the presence of a cuprous compound and metallic copper.

U.S.P. 1,614,584 (Jan. 18, 1927, Roger Adams, J. M. Davidson, and Ivan Gubelmann, Newport Co.), covers the new compound 4-amino-3-nitrobenzoyl-*o*-benzoic acid and a process of making the same.

U.S.P. 1,617,313 (Feb. 8, 1927, H. D. Gibbs and E. L. Frederick, E. I. duPont deNemours & Co), covers a process for producing 1-arylaminonaphthalene-8-sulfonic acid (that is, aryl-peri acid) by heating peri acid and a primary amine under pressure in the presence of water.

U.S.P. 1,619,368 (Mar. 1, 1927, L. S. Pratt, E. H. Weltz, and W. L. Mills, E. I. duPont deNemours & Co.), covers a process for the preparation of alkyl-nitro aryl ethers, for example, *p*-nitrophenetole, *o*-nitroanisole, *p*-nitroanisole or dinitroanisole, which consists in heating a mono- or poly-nitroaryl halide with alcohol and caustic under pressure in the presence of an oxidizing agent such as metallic oxides or potassium ferricyanide or hydrogen peroxide or a gaseous oxidizing agent such as air or oxygen.

SUGGESTIONS FOR RESEARCH

A problem of general interest to all producers of dyes is a study of the fundamental facts underlying the fastness of a color when applied to the fabric, especially fastness to light, washing and chlorine. This must of necessity be preceded by a standardization of fastness tests. We understand that some work is now being done in this country with the idea of establishing standards for fastness. Our universities can be of great assistance to the industry by undertaking to answer such questions as: What is the relation between chemical constitution and fastness to light? Why is the same dye faster to light when applied to cotton than when dyed on silk or wool, or *vice versa*? Is there any relation between the absorption spectra (including the ultraviolet) of dye solutions and the fastness to light? What is the nature of the reactions which take place when a dye fades on exposure to light?

A problem of especial interest to those engaged in the manufacture of azo colors is a study of the reactivity of the diazonium group. For example, the effect of hydrogen ion concentration, temperature, salt concentration, etc., on the reactivity of the diazonium group, and the effect of substituents on such reactivity. Another problem is a study of the rate of coupling. For example, a determination of the relation between the chemical constitution of an end component and its rate of coupling to a given diazonium compound.

Chapter XLVI.

Vat Dyes and Intermediates.

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and
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The outstanding single feature of the report of the U. S. Tariff Commission on the production of dyes in the United States for the year 1926 is the fact that a new record was established in the manufacture of vat dyestuffs with a total output, exclusive of indigo, of more than 4,000,000 pounds. This growth is very striking when this figure is compared with the previous high output of 2,600,000 pounds established in the year 1925. The line of these colors now produced in America has been rapidly increased so that all of the leading colors of this class are now available from a domestic source and other of the more important specialties are in an advanced stage of development. It seems reasonably certain that the time is not far distant when America will be practically independent of imported vat colors.

The rapid growth in the production and use of this class of colors may be ascribed to the following causes: 1. The insistent and increasing demand of the public for "fast dyed" fabrics. 2. The encouragement given by the textile mills to the use of faster and better colors and their ingenuity in developing new and improved methods for the application of these colors. This improvement has been most marked in the printing trade and in the application on piece-goods by the "pad and jig" method. 3. The continuation of aggressive and intensive research work upon the part of the companies engaged in the development and manufacture of these colors. This work has been directed along the line of: a. Improving the quality of the existing types with the goal of producing these colors in a state of as near chemical perfection as is consistent with large scale works production. b. The addition to the line of other colors of this general class to meet the existing needs of the trade. This includes colors already known and not previously manufactured in this country as well as new types to meet the specific demands in shades and properties. c. The finishing of these colors in a physical state most suitable for the various forms of application for which they are intended. 4. Increased efficiency in manufacture as a result of greatly increased production in a more stabilized industry.

While this rapid growth in the manufacture and use of these colors is very gratifying, a survey of the literature for the period covered in this report shows a surprisingly small amount of published information from the research laboratories of this country on the subject of vat colors and their intermediates. The university laboratories have not yet taken advantage of the opportunity offered for interesting and fruitful research in this field. Much of the success of the vat color industry in Germany during the early stages of its development and even up to the present time may be ascribed to the close cooperation between the university and industry in that country. The contributions from the university laboratories made by such men as Friedlander in the field of the thioindigoids and Scholl in the field of the anthraquinone vat colors were an invaluable aid to the German industry. The combined effort of the university laboratories and the research laboratories of the firms engaged in the manufacture of these colors is needed for a thorough and full development in America of this important field.

The meagreness of the literature disclosures from the research laboratories of the American firms engaged in the manufacture of these colors do not afford a true picture of their accomplishments. The greatly increased production of these colors on a commercial scale, the lowered cost at which they are furnished to the consumer, and the improved quality of the products now sold to the trade are largely the result of the laboratory work actively prosecuted at all times on the improvement of chemical methods. Much of this work relates to the commercial phase of production and costs and has remained unpublished.

Of still greater importance to the future of the industry is the active work which has been in progress on the discovery and development of new intermediates and colors. It is known that this work has led to important and valuable results and unquestionably full information regarding the results obtained will be forthcoming when plans have been completed for the manufacture and sale of these new products, and when the proper patent protection has been procured.

In the work on new colors in the industrial laboratories of the American firms engaged in this line of manufacture particular attention has been paid to the development of fast brown shades. This work was conducted primarily to supply the existing need for fast brown vat dyes competitive in shade and properties with the well known Hydron and Algol Browns of foreign manufacture. The Newport Company discovered that by condensing halogen derivatives of pyranthrone with aminoanthraquinones new vat dyes are obtained which dye cotton in full rich brown shades. Other work along the same line by the Newport Company consisted in the condensation of halogenated pyranthrone with carbazol and the condensation of halogenated pyranthrone with aminodibenzanthrone.[1]

The technical importance of the intermediate, benzanthrone, has led to further work on the best method for its manufacture with the object of increasing the yield and improving the quality. In this connection two patents have been granted to the duPont Company; the one consists in a process for producing benzanthrone which comprises treating anthraquinone dissolved in concentrated sulfuric acid with freshly precipitated copper to effect the reduction of anthraquinone to anthranol and subsequently adding glycerine and water to effect the synthesis;[2] the other covers the use of mild oxidizing agents such as anthraquinone or nitrobenzene in the condensation of anthranol with glycerine to produce benzanthrone.[3] A patent has been granted to the National Aniline & Chemical Company for the purification of crude benzanthrone by sublimation.[4] A description is given of the equipment to be used and it is claimed that by proper control of conditions benzanthrone can be separated from the non-sublimable impurities commonly present in the technical product and so obtained in a purified or partially purified state.

A patent was granted to the National Aniline & Chemical Company for the purification of crude anthraquinone by extracting with a hot alkaline solution and separating the resulting solution of impurities from the undissolved purified anthraquinone.[5]

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[1] Gubelmann, U. S. P. 1,596,528, 1,596,529, 1,596,530, 1,596,531 (Aug. 17, 1926).
[2] Peck and Sachs, U. S. P. 1,601,319 (Sept. 28, 1926).
[3] Caswell and Marshall, U. S. P. 1,626,392 (Apr. 26, 1927).
[4] Lyford, U. S. P. 1,591,715 (July 6, 1926).

A new and improved process for the production of the well known 1,2,1′,2′-anthraquinoneazine has been patented by the National Aniline & Chemical Company.[6] The process comprises carrying out the fusion of β-aminoanthraquinone with caustic potash in the presence of an indifferent solvent or diluent such as a high boiling fraction of a mineral oil.

While a number of American patents have been granted in the field of the thioindigoids to the Swiss and German concerns there has been nothing published in this field of strictly American origin. This particular line of vat colors is rapidly growing in importance in the United States. Though not so fast to light as the fastest anthraquinone colors, their relatively easy working properties and unusual fastness to chlorine and light, combined with great brilliancy of shades, have enabled them to take an important place where fastness and brilliancy are desired. The most noteworthy progress in this field has been to extend the range of colors so that today, without a single exception, every important thioindigoid is available from a domestic source.

The foreign laboratories have investigated quite extensively the thioindigoids containing the benzene nucleus and this field has been fairly well covered. At present the tendency seems to be along the line of developing intermediates and colors containing the naphthalene, anthracene, or anthraquinone nucleus. There still remains a number of possibilities along this line and in the direction of development of new methods for the synthesis of thiophenols or aminothiophenols which are the starting materials for the thioindigoids. It is quite possible that when this field is sufficiently cultivated in America there will be discovered a reaction comparable with the very novel method developed by Herz of the Cassella Company whereby a large series of aminothiophenols and thioindigoids could be prepared by the basic reaction of sulfur chloride on various aromatic aminohydrochlorides. In passing it may be mentioned that a study of the reaction of a very cheap material, sulfur chloride, upon a variety of organic compounds would undoubtedly be of very great value.

To promote ease of application it is necessary that the water-insoluble vat colors be produced and retained in a fine state of subdivision. A study of methods for reducing the particle size of these colors to the finest possible state offers an interesting and practical problem in physical chemistry. This study should include the determination of the influence of particle size on the rate of reduction. Furthermore, a physical-chemical study of the affinity of the soluble vat of the colors for the same and different fibers under different conditions of concentration, temperature and alkalinity should yield results of great importance in the technical application of these colors. These problems have been given a great deal of study from the practical standpoint but only a limited amount of scientific work has been done to determine the underlying chemical and physical principles involved and to make use of these in the control of the operations under consideration.

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[5] Lewis, U. S. P. 1,591,712 (July 6, 1926).

[6] Rogers, U. S. P. 1,609,965 (Dec. 7, 1926).

A statistical study of the accuracy of dye testing vat dyestuffs for strength under the usual laboratory conditions has been reported by Draves of the Technical Laboratory of the duPont Company.[7] While the results reported are fairly satisfying as regards the determination of the comparative strength and value of trade products this method of testing does not show the actual purity of the chemical compounds in question and so cannot be used when absolute results are wanted. The development of analytical methods for other vat colors, similar to those now used in the estimation of indigo, would not only serve a useful purpose in standardization but would also furnish the manufacturer with more reliable chemical control in his operations.

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[7] *Am. Dyestuffs Reporter*, **16**, 337 (1927).

Chapter XLVII.

Leather.

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Progress in the chemistry of leather manufacture in America during the past two years compares very favorably with that made in Europe. The greatest efforts have been devoted to a better understanding of the mechanism of the extremely complex reactions involved in tanning.

Raw Skin. Turley [1] demonstrated microscopically that the collagen fibers of skin are enclosed in sheaths of areolar tissue. He also noted a layer 5 microns thick on the grain surface of limed and unhaired steer hide that stained differently from the fibers of the grain membrane and seemed to have properties different from those of the cells of the *stratum germinatum.* This is apparently the elusive hyaline layer whose existence has often been considered imaginary. Many new photomicrographs of cross sections of steer hide at high magnification have been furnished by Turley and by McLaughlin and O'Flaherty.[2]

McLaughlin and Theis [3] found that certain fatty constituents of skin are liberated as a result of post mortem changes, but that this action and the further changes in character of the fat are lessened by prompt curing of the skin. Theis [4] has reported further data on the mineral and fatty constituents of skin.

Merrill [5] showed that calfskin contains a small amount of nitrogenous matter insoluble in water but soluble in dilute sodium chloride solution. The quantity of material dissolved either by water or salt solution approaches a limit with time of extraction. After curing, the quantity of water-soluble nitrogen is doubled while that of nitrogen soluble in salt solution is diminished. Gustavson[6] found the isoelectric point of collagen to be at pH = 5.0, by noting the rise or fall of pH value when hide powder was introduced into chrome liquor with added sodium acetate or formate. Kelly[7] found the nitrogen content of collagen in standard hide powder to be 18.0% and in corium from steer hide 17.9%.

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[1] *J. Am. Leather Chem. Assoc.,* **21**, 117 (1926).
[2] *J. Am. Leather Chem. Assoc.,* **21**, 338 (1926).
[3] *J. Am. Leather Chem. Assoc.,* **21**, 551 (1926).
[4] *J. Am. Leather Chem. Assoc.,* **21**, 622 (1926); **22**, 70 (1927).
[5] *Ind. Eng. Chem.,* **19**, 249 (1927).

Microorganisms and Grubs. Wilson and Daub[8] traced the appearance of freckle-like spots on leather to infection by *Aspergillus niger* and illustrated their findings with photomicrographs. They[9] also illustrated similarly bacterial damages resulting in loose and pipy grain, veiny leather and spots. Frey[10] demonstrated that a very serious grain damage found in certain hides was caused by a mite, *Demodex folliculorum,* acting in the hair follicles. An interesting study of the origin and life cycle of grubs in cattle hides was made by Webb.[11]

Curing. Thomas and Foster[12] found that concentrated solutions of alkali and alkaline earth halides catalyze the hydrolysis of hide substance, whereas concentrated solutions of the corresponding sulfates inhibit hydrolysis, indicating that the sulfate is to be preferred to the chloride, in curing, where enough salt has been used to stop bacterial action. McLaughlin and Theis[13] pointed out that sulfate is not as effective against bacteria as the chloride and that the sulfate dehydrates the skin more rapidly. Thomas and Kelly[14] made the interesting discovery that a mixture of sodium chloride and calcium chloride has a much less destructive action on hide substance than either salt used alone. It appears possible that these two salts form addition compounds less active on hide substance than the simple salts.

Gustavson[15] explained the destructive action of salts on protein on the basis of the well known works of Pfeiffer and Stiasny. Halides form fairly stable addition compounds with amino acids and ketopiperazines, increasing their solubilities greatly, the order of increasing activity of different halides being the same as that of increasing destruction of hide substance found by Thomas and Foster. The halide forms an addition compound with the amino acid or diketopiperazine units making up the protein molecule, increasing their tendency to disperse, with consequent increase in hydrolysis of the protein. His experiments also indicated that the hydrolysis by neutral salts is really only a separation of the groups, or peptones, held together by secondary valency forces and he was able to show that the release of these secondary valency forces influences tannin fixation.

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[6] *J. Intern. Soc. Leather Trades Chem.*, **10**, 203 (1926).
[7] *J. Am. Leather Chem. Assoc.*, **21**, 573 (1926).
[8] *J. Am. Leather Chem. Assoc.*, **20**, 400 (1925).
[9] *Ind. Eng. Chem.*, **17**, 700 (1925).
[10] *J. Am. Leather Chem. Assoc.*, **20**, 373 (1925); **21**, 571 (1926).
[11] *J. Am. Leather Chem. Assoc.*, **20**, 453 (1925).
[12] *Ind. Eng. Chem.*, **17**, 1162 (1925).
[13] *Collegium*, No. **678**, 431 (1926).
[14] *Ind. Eng. Chem.*, **19**, 477 (1927).
[15] *J. Am. Leather Chem. Assoc.*, **21**, 206, 366 (1926).

Soaking. McLaughlin and Rockwell,[16] in a study of the bacteriology of soaking, worked out the principle that the maximum period of soaking should not be longer than the minimum lag period in the growth of the bacteria. McLaughlin and Moore [17] developed some important principles with regard to soaking sheepskins and McLaughlin and Highberger [18] with regard to soaking goatskins.

Unhairing. Merrill [19] discovered the remarkable unhairing properties of stannous chloride by reasoning from the rapidly developing theory of the mechanism of the action of sulfides in liming. The theory is that, when the cystine groupings in the keratin molecule are reduced to cysteine, the altered keratin is much more rapidly hydrolyzed by alkali than the unaltered keratin. He [20] also showed that ammonia is without action on collagen, but is a powerful unhairing agent, with a maximum action at pH = 11.8. Unhairing by ammonia is retarded by the swelling action of lime on the skin.

Bating. Wilson and Merrill [21] found that the important role played by trypsin in bating is the hydrolysis of keratose, a degradation product of keratin, and they [22] developed a method for measuring the bating power of enzyme preparations with considerable accuracy. They [23] also showed how commercial pancreatins differ in their activities on keratose, elastin, collagen, casein and fats. Merrill [24] measured the effect of temperature on bating and showed that the rate of digestion of keratose is doubled for each 10°C. rise in temperature, over the bating range, while the rate of digestion of collagen is increased threefold between 15 and 25° and nineteenfold between 25 and 35°C. Merrill and Fleming [25] showed that trypsin will hydrolyze fresh collagen, but that the amount of collagen hydrolyzed in ordinary bating is negligible.

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[16] *J. Am. Leather Chem. Assoc.*, **20**, 312 (1925).
[17] *J. Am. Leather Chem. Assoc.*, **21**, 274 (1926).
[18] *J. Am. Leather Chem. Assoc.*, **21**, 280 (1926).
[19] *J. Am. Leather Chem. Assoc.*, **22**, 230 (1927).
[20] *Ind. Eng. Chem.*, **19**, 386 (1927).
[21] *Ind. Eng. Chem.*, **18**, 185 (1926).
[22] *J. Am. Leather Chem. Assoc.*, **21**, 2 (1926).
[23] *J. Am. Leather Chem. Assoc.*, **21**, 50 (1926).
[24] *Ind. Eng. Chem.*, **19**, 382 (1927).
[25] *J. Am. Leather Chem. Assoc.*, **22**, 139 (1927).

Vegetable Tanning. Thomas [26] has given further evidence in favor of the chemical nature of vegetable tanning. Thomas and Foster [27] studied the vegetable tanning of deaminized collagen. It showed two points of minimum plumping, at $pH = 4.0$ and 8.3, and swelled in contact with solutions of higher pH value than 6 to a much greater extent than normal collagen. In accordance with the chemical theory of combination, they found that deaminization of collagen caused a decrease in rate of vegetable tanning in acid solution and a shift in the minimum to a more acid region. Thomas and Kelly [28] showed that vegetable tanning in the pH range 8 to 12 is due to the presence of quinone-like substances; with pure tannin there is practically no tanning action at pH values above 8.

Wilson and Bear [29] showed that an increasing degree of tannage results in a lessened capacity of collagen to combine with acids, indicating that tannin and acids become attached to the same protein groups. Page and Gilman [30] demonstrated the applicability of the Wilson-Gallun method to the plumping power of vegetable tan liquors on skin and showed that the plumping of skin in tan liquor is determined by the pH value and valency of the anions present. Frey and Leinbach [31] analyzed the stump wood, root bark, and root wood of the American chestnut tree, *Castanea dentata*, and found them rich in tannin, suggesting their possible commercial utilization.

Chrome Tanning. The science of chrome tanning has been very greatly advanced during the past two years by the remarkable researches of Gustavson,[32] who has practically revolutionized our ideas on the molecular mechanism of chrome tanning. It is impossible to do justice to this work in the short summary allowed in this chapter. Gustavson showed that both cationic and anionic chromium play parts in tanning. The cationic chromium reacts with the acid groups of the protein, according to the older theories, but combination between protein and anionic chromium plays a big part, increasing as the pH value of the chrome liquor is in-

[26] *J. Am. Leather Chem. Assoc.*, **21**, 487 (1926).

[27] *J. Am. Chem. Soc.*, **48**, 489 (1926).

[28] *Ind. Eng. Chem.*, **18**, 625 (1926).

[29] *Ind. Eng. Chem.*, **18**, 84 (1926).

[30] *Ind. Eng. Chem.*, **19**, 251 (1927).

[31] *J. Am. Leather Chem. Assoc.*, 20, 457 (1925).

[32] *J. Am. Leather Chem. Assoc.*, 20, 382, 406, 517, 519 (1925); **21**, 22, 559 (1926); 22, 102, 125, 236 (1927); *Ind. Eng. Chem.*, **17**, 823, 945 (1925); **19**, 81, 243 (1927); *J. Am. Chem. Soc.*, **48**, 2963 (1926).

creased towards the isoelectric point of collagen, where the secondary valency forces of the protein are at a maximum. Apparently molecular compounds are formed, involving the basic nitrogen groups of the protein. Deaminization of collagen causes a decrease in combination with sodium oxalato-chromiate.

Thomas and Kelly[33] found that the rate of combination of chromium with collagen is greatly inhibited by previous tanning with quinone or tannin or by deaminization, indicating a significant role played by the nitrogen groups of the protein. Gustavson explains the diminished rate of fixation of cationic chromium by the lesser fixation by the protein of acid resulting from hydrolysis of the protein salts.

In reply to Orthmann,[34] Wilson and Lines[35] showed that all of the acid sulfate of chrome leather can be removed by washing with water. Gustavson[36] showed, however, that this acid sulfate is present in two states of combination, one directly with the protein and relatively readily hydrolyzable and one with the chromium and difficultly hydrolyzable. Cobb and Hunt[37] made a number of practical observations on chrome tanning; with chrome liquors treated with sodium acetate or formate, they found an increase in rate of tanning with pH value up to about 6.

Other Methods of Tanning. Thomas and Kelly[38] showed that the combination of formaldehyde with protein is not limited to a simple one to one ratio, giving a methyleneamino linkage with the amino nitrogen, but that a triformal linkage with amino groups is also possible. The further combination with imino nitrogen permits the combination of relatively large amounts of formaldehyde with protein. Aldehyde tanning proceeds at a maximum rate in neutral or very faintly alkaline solution.

Thomas[39] studied the so-called sulfur tannage. Fixation of sulfur by collagen from Oden's colloidal sulfur is due to combination between collagen cations and the anion $xS.yS_5O_6H'$ of the complex $xS.yS_5O_6H_2$. The compound is more resistant to the action of cold water than raw collagen, but readily decomposes in hot water. Practically all of the sulfur is extractable by carbon disulfide. He concluded that colloidal sulfur cannot be classed as a tanning agent.

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[33] *J. Am. Leather Chem. Assoc.*, 48, 1312 (1926).
[34] *J. Am. Leather Chem. Assoc.*, 21, 30 (1926).
[35] *J. Am. Leather Chem. Assoc.*, 21, 297 (1926).
[36] *J. Am. Leather Chem. Assoc.*, 21, 559 (1926); 22, 60 (1927).
[37] *J. Am. Leather Chem. Assoc.*, 20, 341 (1925); 21, 454 (1926).
[38] *J. Am. Leather Chem. Assoc.*, 21, 57 (1926).
[39] *Ind. Eng. Chem.*, 18, 259 (1926).

Thomas and Kelly[40] showed that quinone combines with the same groups in the collagen molecule that fix vegetable tannin. In neutral liquors, chlorides retard and sulfates favor quinone tanning.

From a study of oil tannage, Mathur[41] concluded that the basic principle involved is the formation of hydroxy compounds within the fibrous structure of the hide substance and the combination of monohydroxy acids with collagen with the elimination of water.

Wolesensky[42] demonstrated that soft, pliable and strong leather can be produced by tanning with condensation products of the sulfonic acids of monohydroxyphenols with formaldehyde, but the leather yield is low. Greater yields can be obtained with sulfonated phenolformaldehyde resins and still greater yields of leather with a sulfonated phenol-acetaldehyde resin. Condensation products of resorcinol or pyrogallol with formaldehyde or acetaldehyde have very great filling properties.

Wallace and Bowker[43] showed that neutralized and concentrated sulfite cellulose wastes from paper mills are rich in materials capable of tanning animal skin, yielding a very satisfactory leather.

Fatliquoring. Leather is fatliquored by drumming in emulsions of various oils in water. The literature on emulsions has recently been reviewed by Thomas.[44]

Analytical Methods. Among the subjects covered in the development of analytic methods are the determination of water in leather by Veitch and Jarrell;[45] of water in tanning materials by Clarke;[46] of water-soluble material in leather by Mosser;[47] of the astringency of tanning materials by Crede;[48] of the plumping power of tan liquors by Porter;[49] and of the enzymic activity of bating materials by Wilson and Merrill;[50] the effect of pH value on tannin analysis by Rogers;[51] and the extraction of tannin by Williams.[52]

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[40] *Ind. Eng. Chem.*, **18**, 383 (1926).
[41] *J. Am. Leather Chem. Assoc.*, **22**, 2 (1927).
[42] Bur. of Standards, *Tech. Papers*, **20**, 1, 275, 519, 529 (1925-6).
[43] Bur. of Standards, *Tech. Papers*, **21**, 309 (1927).
[44] *J. Am. Leather Chem. Assoc.*, **22**, 171 (1927).
[45] *J. Am. Leather Chem. Assoc.*, **20**, 334 (1925); **21**, 435 (1926).
[46] *J. Am. Leather Chem. Assoc.*, **21**, 385 (1926).
[47] *J. Am. Leather Chem. Assoc.*, **20**, 378 (1925; **21**, 306 (1926).
[48] *J. Am. Leather Chem. Assoc.*, **20**, 573 (1925).
[49] *J. Am. Leather Chem. Assoc.*, **21**, 425 (1926).
[50] *J. Am. Leather Chem. Assoc.*, **21**, 2 (1926).
[51] *J. Am. Leather Chem. Assoc.*, **20**, 370 (1925).
[52] *J. Am. Leather Chem. Assoc.*, **22**, 97 (1927).

Properties of Leather. During the past two years the first serious attempt was made to measure and catalog systematically the important properties of the typical leathers of the market. Wilson and his collaborators selected representative samples of 18 different kinds of leather, of which Wilson and Daub[53] published photomicrographs of cross sections; Wilson and Lines[54] the chemical composition; Wilson and Guettler[55] measured the ventilating properties; Wilson and Daub[56] the tensile strength, stretch and stitch tear; and Wilson and Kern the resilience[57] and the contraction and expansion with relative humidity.[58]

The destructive action of acids upon leather has been studied by Veitch, Frey and Leinbach,[59] by Wilson,[60] and by Wilson and Kern.[61] When insufficiently protected, leathers pick up acids from polluted city atmospheres and suffer deterioration with time. Wilson showed that chrome leather has a greater capacity for combining with sulfuric acid and is much more readily destroyed by the free acid than vegetable tanned leather. The resistance of chrome leather to the destructive action of sulfuric acid can be increased by retanning it with vegetable tanning materials. Very thin sheets of leather can be made by coating the surface of chrome leather with vegetable tannin and then dissolving away all but the tannin coated surface with 3-molar sulfuric acid solution. It is only the volatility of hydrochloric acid that makes its presence in leather less harmful than sulfuric acid. Wilson and Kern made the surprising discovery that the destruction of leather by acid increases with the relative humidity of the atmosphere with which it is in equilibrium.

Wilson and Kern studied the effect upon strength and stretch of degree of splitting,[62] of relative humidity,[63] and of location upon the skin.[64] In a study of the effect of color upon the absorption of heat by leather in sunlight, Wilson and Diener[65] found that a black leather becomes 9°C. warmer than a very light colored tan.

[53] *J. Am. Leather Chem. Assoc.*, **21**, 193 (1926).
[54] *J. Am. Leather Chem. Assoc.*, **21**, 198 (1926).
[55] *J. Am. Leather Chem. Assoc.*, **21**, 241 (1926).
[56] *J. Am. Leather Chem. Assoc.*, **21**, 294 (1926).
[57] *J. Am. Leather Chem. Assoc.*, **20**, 576 (1925); **21**, 399 (1926).
[58] *J. Am. Leather Chem. Assoc.*, **21**, 351 (1926).
[59] *J. Am. Leather Chem. Assoc.*, **21**, 156 (1926).
[60] *Ind. Eng. Chem.*, **18**, 47 (1926).
[61] *Ind. Eng. Chem.*, **19**, 115 (1927).
[62] *Ind. Eng. Chem.*, **18**, 312 (1926).
[63] *J. Am. Leather Chem. Assoc.*, **21**, 250 (1926).
[64] *Ind. Eng. Chem.*, **17**, 829 (1925).
[65] *Hide and Leather*, **73**, no. 23, 39 (1927).

Chapter XLVIII.

Rubber.

William C. Geer,

Formerly Vice President, The B. F. Goodrich Co.

Research on rubber extends over a wide range, involving, as it does, the organic chemistry of an intricate hydrocarbon on the one hand, and the practical testing of a multitude of rubber articles of utility, on the other. A logical beginning of a review is with the work that has been done on the fundamental conceptions.

Dinsmore,[1] in reporting on the structure and composition of Hevea rubber, finds all attempts to arrive at a definite conception of the structure of rubber fruitless. He feels that we are not positive as to how the isoprene units are connected to form the rubber molecule, nor do we know in what way the molecules are tied together in structural formation. Here is still a fine field for research, and the writer is inclined to believe that it may be necessary for us to alter our conception of fundamental molecular structure in order to explain rubber.

Hauser,[2] at the meeting of the American Chemical Society, showed a film upon which was recorded a dissection of the rubber latex particle which is suggestive, and is mentioned here for that purpose, even though not an American research. It would be well for American chemists to read the papers by Stevens,[3] De Vries,[4] and Van Rossem and Dekker,[5] if for no other reason than to gain an idea of the degree to which research on the problems on crude rubber is conducted across the water.

Some day this country will possess a large and well established crude rubber plantation for McCallum,[6] Carnahan[7] and Spence[8] have reported upon the results of years of research in the south of California on the growing of the guayule shrub. They stimulate us to look forward to the time when some square miles of California land will produce a healthy percentage of our rubber needs. These developments are supported by chemical and botanical research of a high order. That the State of California is not backward is also to be noticed in the establishment of the California Botanical Gardens near Los Angeles, which is about to begin work on the cultivation of American growing rubber bearing trees and shrubs.[9]

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[1] *Ind. Eng. Chem.*, **18**, 1140 (1926).
[2] *Ind. Eng. Chem.*, **18**, 1146 (1926).
[3] *Ind. Eng. Chem.*, **18**, 1116 (1926).
[4] *Ind. Eng. Chem.*, **18**, 1129 (1926).
[5] *Ind. Eng. Chem.*, **18**, 1152 (1926).
[6] McCallum, *Ind. Eng. Chem.*, **18**, 1121 (1926).
[7] Carnahan, *Ind. Eng. Chem.*, **18**, 1124 (1926).
[8] Spence, *Ind. Eng. Chem.*, **18**, 1126 (1926).

Kemp[10] has done further work on the direct determination of the hydrocarbon in raw rubber, balata and related substances. Using iodinechloride in glacial acetic acid he determined the unsaturation of the hydrocarbon in rubber and balata and found that the analyses correspond closely to the theoretical values.

Clark[11] has applied the X-ray methods of study to raw and vulcanized rubber and finds, as have some European observers, that unstretched raw rubber is amorphous, and that on stretching it becomes crystalline; the computations indicate the unit rubber crystal to be $(C_5H_8)_4$, with some allowance for uncertainties due to the complexities of the problem.

Although not strictly in the field of research, those interested in rubber will find an article by Whitford[12] on the possibilities of the plantation industry to be stimulating and likewise an article by Bicknell.[13]

Synthetic rubber still seems to be in the stage of discussion in this country. Weber[14] talked about it; Weil[15] told of the German experiences; Burgdorf[16] feels optimistic over its future; while Geer[17] thinks that the plantation will always produce rubber much cheaper than can the chemist. Calvert[18] describes a series of experiments leading to the preparation of dimethylbutadiene from acetone. They are quite casual and incomplete. Synthetic rubber demands close work of an exacting character and one may remark that we had better stop talking and let the laboratory men produce.

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[9] Merrill, *India Rubber World*, **76**, 132 (1927).
[10] *Ind. Eng. Chem.*, **19**, 531 (1927).
[11] *Ind. Eng. Chem.*, **18**, 1131 (1926).
[12] *Ind. Eng. Chem.*, **18**, 1113 (1926).
[13] *Ind. Eng. Chem.*, **18**, 1109 (1926).
[14] *Rubber Age* (N. Y.), **19**, 493 (1926).
[15] *Ind. Eng. Chem.*, **18**, 1174 (1926).
[16] *Ind. Eng. Chem.*, **18**, 1172 (1926).
[17] *Ind. Eng. Chem.*, **18**, 1136 (1926).
[18] *India Rubber and Tire Review*, **26**, no. 9, 48 (1926).

In the reclaimed rubber field there has been nothing of a new or important character published. There has been a good deal of talk such as that by Bierer[19] before the Institution of the Rubber Industry (London), who, quite ill advisedly, advocates greater use of reclaimed rubber. Winkelmann[20] has given few specific data on the properties of certain grades of reclaimed rubber. The Department of Commerce[21] in a valuable report prepared tabular data which show the fact that reclaimed rubber has now come to be used to the extent of 164,000 tons in 1926 and that was 45% of the amount of crude rubber used.

In the field of colloid chemistry some good research work was done on rubber. Gibbons and Hazell[22] said that, when a pure rubber is dissolved to a sol in organic liquids, contraction occurs. Whitby[23] studied the relation between the chemical character of the organophilic colloids and that of the liquids which they imbibe. He summarizes the work on some 350 solvents. It is an admirable study and too long and detailed to review with satisfaction to the reader.

Sheppard[24] has reviewed his work on the electrodeposition of rubber, and Schade[25] described some of the commercial possibilities of the process. These reviews are of interest to anyone desiring to begin some research work on this subject, in which field there is still a fine opportunity. A new application of latex is its use in cement for sealing tin cans for food containers as promoted by Dewey and Almy.[26] Here again is a suggestive development.

Powers[27] contributed a review of the contributions of the dyestuff industry to rubber, including a discussion of accelerators, antioxidants and colors. The latter is new and the duPont Company has brought out some remarkable colors.

Whitby and Greenberg[28] show that the resin constituents of raw rubber play an important part in vulcanization. This field of research has a bearing on the theory of vulcanization.

The accelerator work of the American rubber chemists usually comes before the public in the form of patent literature, of which

[19] *India Rubber and Tire Review*, **27**, 44 (1927).
[20] *Ind. Eng. Chem.*, **18**, 1163 (1926).
[21] *Rubber Age* (N. Y.), **20**, 165 (1927).
[22] *J. Am. Chem. Soc.*, **49**, 620 (1927).
[23] Colloid Symposium Monograph, 4, 203 (1926).
[24] *Rubber Age* (N. Y.), **21**, 76 (1927).
[25] *Rubber Age* (N. Y.), **21**, 79 (1927).
[26] *India Rubber World*, **75**, 185 (1926).
[27] *Ind. Eng. Chem.*, **18**, 1344 (1926).
[28] *Ind. Eng. Chem.*, **18**, 1168 (1926).

there is a large group. Elley and Powers [29] have reviewed these patents so far as they cover the guanidines. This group is one of the largest in point of number of pounds consumed, but as yet there seems to be no satisfactory explanation of their activity. Trickey and Leuck [30] review the literature on furfural derivatives as accelerators, which derivatives have not been studied thoroughly, but seem to be less active than the guanidines.

Anti-oxidants are substances which, when added to rubber mixtures, prevent the decay of the vulcanized article on standing. This is one of the great fields for detailed rubber research, although there are several well known and quite useful substances on the market. Weber [31] mentions them and Elley and Powers [29] give some of the results to be expected from their use. White and Boone [32] contribute an interesting series of data on the effect of fatty acids on the tensile strength and elongation of vulcanized rubber mixtures and show the relation between fatty acids of different melting points and heats of crystallization with respect to their effect upon the tensile strength and elongation of the vulcanizates.

Studies of pigments are going on and it is to be hoped that some day the reason for the various action of these substances will come to light. Meanwhile the chemist interested in rubber would do well to watch the efforts of the paint chemists with respect to his particle size investigations. Some valuable data along this line have been reported by Stutz and Pfund,[33] Green and Haslam [34] and Calbeck and Harner.[35]

The effect of numerous substances upon the properties of vulcanized rubber of several different compositions has been investigated by a few chemists. Depew and Lewis [36] show that some compositions containing acid-soluble oxides are not deteriorated in contact with sulfuric acid to above 50% concentration, concentrated HCl or concentrated NaOH. In one of the best pieces of research work of the year Lowry and Kohman [37] show the mechanism of the absorption of water by rubber. Tests were made with uncured and cured rubber, gutta percha and balata in NaCl solutions. They worked out the data on vapor pressure of the water, water-soluble constituents, state of the water external to the rubber, combined sulfur content, temperature, hydrostatic pressure on the rubber, and the effect of aging of the rubber upon its water solubility. Co-related with this research was one by Williams and Kemp [38] on a study of rubber for submarine cable insulation in which they found that the absorption of water by gutta percha and rubber depends upon the salt content of the water and upon the water-absorbing constituents within the sample.

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[29] *India Rubber World*, **75**, 143 (1926).
[30] *Ind. Eng. Chem.*, **18**, 812 (1926).
[31] *Ind. Eng. Chem.*, **18**, 963 (1926).
[32] *Ind. Eng. Chem.*, **19**, 398 (1927).
[33] *Ind. Eng. Chem.*, **19**, 51 (1927).
[34] *Ind. Eng. Chem.*, **19**, 53 (1927).
[35] *Ind. Eng. Chem.*, **19**, 58 (1927).
[36] *India Rubber World*, **75**, 129 (1926).
[37] *J. Phys. Chem.*, **31**, 23 (1927).

A machine for the measurement of the resistance of rubber samples to abrasive wear has been offered by Williams.[39] This is one of many such machines, no one of which has yet received even a majority adoption. Evidently why rubber wears out when subjected to service as on a tire is still an unsolved problem.

Boggs,[40] who has long been known as the discoverer and advocate of selenium in rubber vulcanization, has published a review and elaboration of his work with Follansbee. No hard rubber is produced with selenium, but only a soft rubber which resists abrasion surprisingly well.

The effect of rubber in the life of cord tire fabric under strain and flexure is recorded by Stavely and Shepard,[41] who find that a cord when well impregnated with a rubber cement flexes a longer time before breaking than one not so treated. The paper, however is incomplete and cannot be called other than a minor contribution to the vast problem of the relation of rubber to cotton in an automobile tire.

The electrical properties of certain rubber sulfur compounds are reported in Technical News Bulletin No. 119 of the Bureau of Standards and, like all pre-publications, is indecisive and scarcely a credit to that great bureau.

In rereading this review one is impressed by two facts: first, that the universities do but little work in the rubber field and second, that the industries do not publish nearly the volume of data that could be reported, judging from the wealth of research work known to be under way. This review is one of publications primarily rather than of data in the hope that those who read it may be stimulated to indulge in the delights of study in a realm of science with a large literature and as yet unsolved.

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[38] *J. Franklin Inst.*, **203**, 35 (1926); *India Rubber J.*, **73**, 277, 317, 403 (1927).
[39] *Ind. Eng. Chem.*, **19**, 674 (1927).
[40] *Trans. Inst. Rubber Industry*, **2**, 272 (1926).
[41] *Ind. Eng. Chem.*, **19**, 296 (1927).

Chapter XLIX.

Cooperative Research Between Industries and Universities.

William J. Hale,

Chairman, Division of Chemistry and Chemical Technology,
National Research Council

In the first volume of this series under this heading there was presented a plan for promoting cooperative researches between industries and universities. It is now appropriate that we give a brief résumé of the researches actually undertaken under this plan.

These researches were instituted during the preceding year, or that year covered by Volume I of this series. The results so far obtained are recorded as of the close of the present fiscal year, or that period covered by this volume.

In the summer of 1925 a thousand or more letters were sent to instructors in chemistry throughout our colleges and universities. A hundred responses indicated a willingness to enter into this form of cooperation. From the industries the Chairman of the Division had secured about two hundred problems carrying with them the promise of financial commitments if the investigators could show any hope of progress.

The difficulty of fitting a problem to a man was most apparent. Nevertheless, there were twenty-five actual researches set into operation by the fall of 1926. The list of these researches is given below.

1. A study of soldering methods as applied to copper bronzes.
2. Determination of butyl alcohol in presence of ethyl alcohol, acetone and butyl butyrate.
3. A study of pyrogallol crystals.
4. A study of mercuric chloride crystals.
5. Determination of solubility of carbon dioxide in acetone and other organic solvents between the temperatures of –80 and 25° C.

6. Investigation of reaction of carbon dioxide upon acetone at high temperatures.
7. A study to improve process for manufacture of mesitylene from acetone.
8. A study of the evaporation of sodium sulfite liquors.
9. A study of method for separation of butyl alcohol, butyl aldehyde, acetone and isopropyl alcohol.
10. Synthesis of hexyl alcohol.
11. Study of alloys that might possibly resist action of sulfur vapors.
12. Determination of relative ethylating powers of sodium ethyl sulfate, ethyl chloride and ethyl bromide with reference to phenol.
13. A study of oxidation of aniline.
14. A study of electrolytic oxidation of benzene.
15. A study of catalytic material employed in manufacture of sulfuric acid by contact process.
16. A study of oxidation products of ethyl alcohol.
17. Detection of traces of cadmium in presence of zinc.
18. Action of certain catalysts on the hydrolysis of halogenated benzene hydrocarbons under pressure.
19. Behavior of tantalum toward various gases at varying temperatures.
20. Synthesis of normal octane.
21. Physico-chemical studies of components in satin white.
22. A study of electrolytic deposition of zinc from zinc sulfate solutions.
23. A method for removal of pinenes from hydrocarbon mixtures.
24. Determination of relative degrees of toxicity as displayed by methyl bromide and methyl chloride in comparison with similar effects of ethyl bromide and ethyl chloride.
25. The action of various metals on halogenated aliphatic acids.

The names of the investigators as well as the names of the industries interested in the problems are not to be given out. The investigators were made acquainted with the industries concerned only after appreciable progress had been reported; shortly thereafter it became the duty of the investigator and the particular industry to deal solely and directly with each other.

The problems are seen to cover a wide range in the chemical field and certainly as wide a field territorially as this country would permit. Correspondence with distant laboratory centers, however, did not materially handicap progress.

Of these twenty-five researches we may now list seven as failures as far as financial recompense was concerned. Of these seven, two problems were outright failures; two reported in short order negative results, which drove the problems from further consideration; three ran into results anticipated by other research workers and about to be made public.

Thirteen of the problems are still under study. Five of the problems have turned out successfully and are closed as far as the Division of Chemistry and Chemical Technology is concerned. In this group fall two cases where the investigators have taken leave of absence from their universities and entered industrial laboratories in order to pursue their researches under better facilities. From this group two patent applications have been filed.

The energy displayed by the great number of these investigators calls for unstinted praise. They have improved themselves and have contributed in no small degree to the good name of their institution. Through some of these researches we have reason to believe that the colleges concerned will see the importance of installing better and better laboratory equipment. It is this factor in particular that has contributed to slowness of progress and ofttimes has actually made advance impossible.

The young chemists in our colleges and universities display a zeal that is admirable. They are keenly alert and intent upon showing their prowess; their colleges, however, and in some cases universities, are living a generation behind the times. The laboratory facilities for chemical studies in colleges and universities, outside of the leading institutions, are abominable and a disgrace to learning. Among the leading institutions our contact has certainly proved that here too the great majority are not keeping abreast of the times. Their young research men are deluged with clerical duties such that little, if any, free time for research is available. Certainly the future standing of our universities will depend more and more upon their scientific attainments. It is well now that they take heed and mend their ways if they would hold the respect of scientific men.

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